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# Research and Development

RATES OF REACTION AND

PROCESS DESIGN DATA FOR

THE HYDROCARB PROCESS

## Prepared for

Office of Policy, Planning and Evaluation

## Prepared by

Air and Energy Engineering Research
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Meyer Steinberg, Atsushi Kobayashi and Yuanji Dong

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Brookhaven National Laboratory
Upton, NY 11973

Hydrocarb Corporation
232 West 40th Street
New York, NY 10018

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In support of studies for developing the coprocessing of fossil fuels with biomass by the Hydrocarb Process, experimental and process design data are reported. The experimental work includes the hydropryolysis of biomass and the thermal decomposition of methane in a tubular reactor. The rates of reaction and conversion were obtained at temperature and pressure conditions pertaining to a Hydrocarb process design. A Process Simulation Computer Model was used to design the process and obtain complete energy and mass balances. Multiple feedstocks includes biomass with natural gas and biomass with coal were evaluated. Additional feedstocks including sewage sludge and digester gas were also evaluated for a pilot plant unit.

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# RATES OF REACTION AND PROCESS DESIGN DATA
# FOR THE HYDROCARB PROCESS

by

Meyer Steinberg and Atsushi Kobayashi
Brookhaven National Laboratory
Upton, NY 11973

and

Yuanji Dong
Hydrocarb Corporation
232 West 40th Street
New York, NY 10018

Prepared For:
U.S. Environmental Protection Agency
Office of Research and Development
Washington, DC 20460

# ABSTRACT

In support of studies for developing the coprocessing of fossil fuels with biomass by the Hydrocarb Process, experimental and process design data are reported. The experimental work includes the hydropryolysis of biomass and the thermal decomposition of methane in a tubular reactor. The rates of reaction and conversion were obtained at temperature and pressure conditions pertaining to a Hydrocarb Process design. A Process Simulation Computer Model was used to design the process and obtain complete energy and mass balances. Multiple feedstocks including biomass with natural gas and biomass with coal were evaluated.

Additional feedstocks including sewage sludge and digester gas were also evaluated for a pilot plant unit.

# CONTENTS

# TABLES

# ACKNOWLEDGEMENT

# METRIC CONVERSION FACTORS

Readers more familiar with the metric system my use the following factors to convert the non-metric units used in this report:

| Nonmentric | Times | Yields Metric |
|---|---|---|
| atm | 101.3 | kPa |
| bar | 100 | kPa |
| Btu/ft$^3$ | 37,233 | J/m$^3$ |
| Btu/gal. | 278.5 | J/liter |
| Btu/lb | 2324 | J/kg |
| ft | 0.3048 | m |
| ft$^3$ | 0.02832 | m$^3$ |
| gal. | 3.785 | liter |
| lb | 0.4536 | kg |
| ton | 907.2 | kg |
| Btu/lb mol | 2.32 | J/g  mol |
| kcal | 4.183 | kJ |
| Btu | 1.06 | kJ |
| psi | 6.89 | kPa |

# ABBREVIATIONS

HPR – Hydropyrolysis reactor
HGR – Hydrogasifier reactor; HPR and HGR are equivalent
MPR – Methane pyrolysis reactor
BTX – Benzene, toluene and xylene
HCSP – Hydrocarb process simulation program
FHP – Flash hydropyrolysis
MTG – Methanol to gasoline process
MSW – Municipal solid waste
PDU – Process demonstration unit

# Part O

## SUMMARY

A feasibility study for the coprocessing of fossil fuels with biomass by the Hydrocarb process was performed for the U.S. Environmental Protection Agency and a report (EPA-600/7-91-007) was issued dated November 1991, entitled "A Feasibility Study for the Coprocessing of Fossil Fuels with Biomass by the Hydrocarb Process." The results of this study indicated technical and economic feasibility compared to conventional processes for converting carbonaceous feedstocks such as coal, natural gas and biomass to clean carbon and methanol fuels. For purposes of mitigating the global greenhouse $CO_2$ problem, coprocessing fossil fuels with biomass, sequestering all or part of the carbon and mainly utilizing the methanol as a power or transportation fuel, presents the option of reducing and eliminating $CO_2$ emissions to the atmosphere while still employing the world's fossil fuel resources. The report recommended that additional confirmation be obtained of the kinetics of the major steps in the Hydrocarb process, which includes the hydropyrolysis of biomass and the thermal decomposition of the methane-rich process gas. To this end, an experimental study was undertaken using the Brookhaven National Laboratory's Tubular Reactor Facility.

In addition to the experimental work, it was recommended that further process design studies be performed employing the Process Simulation Computer Model developed by the Hydrocarb Corporation with alternative carbonaceous feedstocks. This report describes the experimental and process design work.

The report is divided into three sections. Part I deals with the hydropyrolysis of biomass. Part II deals with the thermal decomposition of methane in a tubular reactor, and Part III gives the results of an analysis of the Hydrocarb process with alternative and multiple feedstocks. The following is a summary of all three parts.

The pyrolysis and hydropyrolysis of biomass was investigated in the tubular reactor facility. Experimental runs with poplar wood sawdust were performed using the tubular

reactor having dimensions 25.4 mm inside diameter and 2.44 m long heated to temperatures of 800°C and pressures between 30 and 5C tm. At low heat-up rate, the reaction proceeds in two steps. First pyrolysis takes place at temperatures of 300 to 400°C and then hydropyrolysis takes place at 700°C and above. This is also confirmed by pressurized thermogravimetric analysis (PTGA). Under conditions of rapid heat-up at higher temper tures and higher hydrogen pressure, gasification and hydrogasification of biomass is es cially effective in producing carbon monoxide and methane. An overall conversion of 88 to 90 wt% of biomass was obtained. This is in agreement with previous work on flash pyrolysis and hydropyrolysis of biomass under rapid heat-up and short reaction residence time conditions. Initial rates of biomass conversion indicate that the rate increases significantly with increase in hydrogen pressure. At 800°C and 51.3 atm the initial rate of biomass conversion to gases is found to be 92% per min.

The reaction rate of methane decomposition using a tubular reactor having a 25.4 mm inside diameter with an 2.44 m long heated zone using the same tubular reactor facility was investigated in the temperature range of 700 to 900°C with pressures ranging from 28.2 to 56.1 atm. The rate is represented by a conventional model, $\frac{-dC_{CH4}}{dt} = k\, C_{CH4}$, where C is the molar concentration and k is the rate constant. When initial $H_2$ concentration is zero, the activation energy for methane decomposition is 31.3 kcal/mol, as determined by an Arrhenius Plot. This value is lower than for previously published results for methane decomposition and appears to indicate that the high-surface-area submicron carbon particles found adhering to the inside of the reactor tend to catalyze the methane decomposition. The e constant has been found to be approximately constant at 900°C in the pressure range investigated. The rate of methane decomposition increases with methane partial pressure to the first-order. The conclusion is reached that the rate of methane decomposition is favored by higher temperatures and pressures while the thermochemical equili m of methane decomposition is favored by lower pressures.

The designed performance of the Hydrocarb process with alternative and multiple feedstocks was investigated. The alternative feedstocks studied for the Hydrocarb process included biomass (wood), Alaska Beluga (sub-bituminous) coal Kentucky (bituminous) coal, North Dakota (lignite) coal and Wyodak (sub-bituminous) coal. A Process Simulation Computer Model was used to design the process, and obtain complete energy and mass balances. Boundary conditions of pressure, temperature and mass balances for the cyclical process were determined. The study also included using sludge and digester gas from sewage plants as additional feedstocks. It was found that these feedstocks have to be coprocessed with either biomass or coal to obtain a workable mass balance. The maximum allowable feed ratios of sludge to biomass or sludge to coal were determined. The effect of pressure and temperature for the biomass and sludge feedstock cases were also developed.

**Part I**

# HYDROPYROLYSIS OF BIOMASS

ATSUSHI KOBAYASHI AND MEYER STEINBERG

BROOKHAVEN NATIONAL LABORATORY
Upton, Long Island, NY, 11973

# Hydropyrolysis of Biomass

by

Atsushi Kobayashi and Meyer Steinberg

Brookhaven National Laboratory

Upton, New York, 11973

## ABSTRACT

The pyrolysis and hydropyrolysis of biomass was investigated. Experimental runs using the biomass (Poplar wood sawdust) were performed using a tubular reactor of dimensions 25.4 mm inside diameter and 2.44 m long heated at a temperature of 800 C and pressures between 30 and 50 atm. At low heat-up rate the reaction procedes in two steps. First pyrolysis takes place at temperatures of 300 to 400 C and subsequent hydropyrolysis takes place at 700 C and above. This was confirmed by pressurized thermogravimetric analysis (PTGA). Under conditions of rapid heat-up at higher temperatures and higher hydrogen pressure gasification and hydrogasification of biomass is especially effective in producing carbon monoxide and methane. An overall conversion of 88 to 90 wt% of biomass was obtained. This value is in agreement with the previous work of flash pyrolysis and hydropyrolysis of biomass for rapid heat-up and short residence time. Initial rates of biomass conversion indicate that the rate increases significantly with increase in hydrogen pressure. At 800 C and 52.4 atm the initial rate of biomass conversion to gases is 0.92 l/min.

# INTRODUCTION

The Hydrocarb Process involves two main reactions; (1)hydrogasification of the carbonaceous feedstock to produce methane-rich gas, and (2)the thermal decomposition of methane to produce hydrogen-rich gas, which is recycled to the hydrogasification section, and finally produces clean carbon black as product.[I-1] A third step combines the CO formed from the hydrogasification section with hydrogen and produces methanol as co-product. The hydrogasification step is important in this process because the composition and the rate of formation of the methane-rich gas can determine the performance of the methane decomposition and methanol reactors as well as the overall performance of the cyclical Hydrocarb Process.

This work was performed in order to investigate both the rate and degree of conversion for the pyrolysis and hydropylolysis of biomass using a tubular reactor at a temperature of 800 C and at pressures of 30 to 50 atm in a hydrogen atmosphere. Data at higher loading densities of biomass compared to previous experiments were also investigated. Previous experiments were performed under flash hydropyrolysis conditions in dilute phase at low $CH_4$, CO, and $CO_2$ in the gaseous phase.[I-2,I-3]

# EXPERIMENTAL DESCRIPTION

## BIOMASS PRET\RATION

The biomass, essentially Poplar wood sawdust, is ground and sieved to less than 150 micron diameter. This particle size was chosen in order that the external heat and gaseous hydrogen in the reactor could penetrate through the biomass particles easily and the biomass could be smoothly fed into the tubular reactor from the feeder attached to the top of the reactor. The ground biomass is first dried in an oven, in which the temperature is kept constant at about 100 C until the moisture content of the biomass is reduced to less than 3 wt% so that the effect of water on the rate of the hydropyrolysis reaction is minimized. The dried biomass component was analyzed by standard analytical procedure and the elemental analysis is shown in Table I-1.

**TABLE I-1.** BIOMASS (POPLAR SAWDUST) COMPOSITION

| Component | Weight Percentage |
|-----------|-------------------|
| C | 51.32 |
| H | 6.16 |
| N | 1.18 |
| S | 0.13 |
| O | 34.57 |
| Ash | 6.64 |
| | 100 wt% (total) |

A very fine silica flour (Cab-O-Sil) was mixed with the ground biomass to prevent agglomeration and allow smooth flow of the sawdust from the feeder into the reactor. This process also prevented plugging inside the reactor. The weight content of silica flour was fixed at about 20 wt% as determined from past experience.[I-2,I-3]

## EXPERIMENTAL PROCEDURE

Figure I-1 shows the schematic flow sheet of the experimental equipment which consists of a biomass feeder, a tubular reactor, a carbon trap, and a gas-chromatograph. Experiments were performed under two different modes; (1) In the first mode of operation, the biomass was

loaded into the reactor on top of a 50.8 mm height of packing consisting of 3.18 mm alumina balls which rests on a perforated disk made of stainless steel positioned at the bottom of the reactor. After a helium purge, hydrogen was introduced into the system up to 52.4 atm and heated up from room temperature to 800 C by the external electrical clamshell heaters. The pressure in the reactor was monitored by a pressure gauge and the concentrations of the effluent carbon containing gases, $CH_4$, $C_2H_4$, $C_2H_6$, CO, and $CO_2$, were analyzed with the thermal conductivity detector in the on-line gas-chromatograph; (2) In the second mode of operation, the reactor temperature was raised to 800 C and the reactor was pressurized with hydrogen over the range 32.0 to 52.4 atm, and the biomass was fed into the reactor at a rate between 10 and 20 grams/min. The pressure in the reactor was monitored and the effluent gases were analyzed in the same manner as mentioned.

The reactor was a 25.4 mm diameter Inconel 617 tube with 6.35mm wall thickness. The total tube height was 3.35 m of which 2.44 m is heated externally with electrical clamshell heaters. As described earlier, it had a disk of stainless steel positioned 0.61 m up from the bottom of the heated zone to act as a hold-up platform for the biomass, and 3.18 mm alumina balls about 50.8 mm in height is also set on the disk to assist in holding the biomass sawdust. The sawdust bed height ranges from 1.52 to 1.83 m in the heated zone.

## EXPERIMENTAL RESULT AND DISCUSSION

Data Table I-1 and Figure I-2 show the results of the experimental Run No. 1154 for the conditions of biomass and hydrogen preloaded into the reactor, system purge and heated up from room temperature to 800 C at an initial pressure of 52.4 atm. The temperature and the concentrations of the gases generated are plotted as a function of the run time and are shown in Figure I-2. At first, CO and $CO_2$ gases are generated before $CH_4$ is formed. The volume of $CO_2$ generated is much larger than CO at the beginning of the run. These gases begin to form around 470 C. $CH_4$ also begins to generate slowly around 470 C and it rapidly increases above 700 C. This phenomena appears to indicate that pyrolysis of biomass starts around 470 C and hydropyrolysis starts about 700 C.

A pressure calibration run is shown in Figure I-3 which indicates the pressure change in the reactor with the temperature for the above mentioned conditions. The dotted line in the figure indicates the calibration line with hydrogen pressure as the reactor is heated up in the same manner as in the run when the biomass was present. This is compared with the pressure change for the Run No. 1154 when the biomass was present as shown by the solid line. At approximately 300 C, the pressure increases sharply compared with the calibration line. The difference between solid line and dotted line indicates that a reaction has occurred in the biomass itself or between the heated biomass and the gaseous hydrogen. As indicated by the composition of the gases generated, CO, $CO_2$, $CH_4$, and others, as shown in Figure I-2, the pyrolysis of the biomass begins around 300 C. Above 400 C, there appears to be almost no change in pressure shown in Figure I-3. However taking into account the data shown in Figure I-2, certainly some gases are generated in that temperature range. A zero pressure change in this region would mean that there is a balance between the gases generated and the hydrogen consumed by hydropyrolysis. Taking this effect into account, pyrolysis and hydropyrolysis of the biomass can be totally represented by following two steps;

First Step ; Pyrolysis of

$$Biomass \xrightarrow{heat} CO + CO_2 + H_2O$$

at temperatures of 300 − 400 C
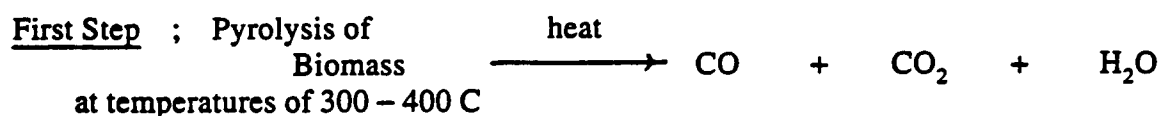
Second Step ; Hydropyrolysis of

$$Biomass + H_2 \longrightarrow CH_4$$
$$C + H_2 \longrightarrow CH_4 + other$$

(remaining char or carbon)                     hydrocarbons

at temperature above 700 C
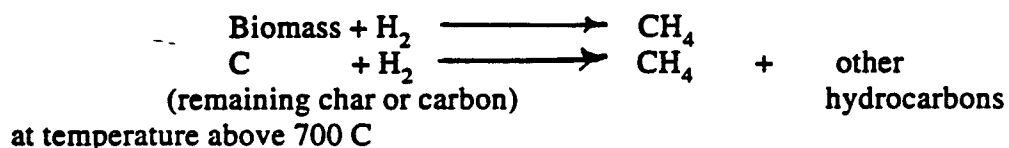
In the first step, at the lower temperatures of 300 through 400 C pyrolysis of the biomass occurs in the early stage of the reaction to produce mainly CO and $CO_2$. In the subsequent step, at higher temperatures above 700 C and at elevated hydrogen pressure, $CH_4$ and some higher hydrocarbons are generated by hydropyrolysis.

In connection with this work R. Khan[1-4] performed two pressurized thermogravimetric analyses (PTGA) for us on Poplar and Fir wood. The PTGA data are shown in Figures I-4 and I-5 at 28.2 atm in helium (solid line) and hydrogen (dotted line) atmospheres. The hydrogen line for weight loss in Figure I-4 for Poplar wood shows 3 steps. The first weight loss of about 10 wt% takes place at the temperature of 150 to 300 C, which is probably due to water vaporization from the biomass. A large second weight loss of about 55 wt% starts at approximately 300 C and continues to about 450 C. Up to 450 C, both the helium and hydrogen curves are very similar. Thus in the low temperature regime, the pyrolysis reaction in the biomass occurs independent of the atmosphere present. On the other hand, beyond this temperature region, the hydrogen atomosphere data line decreases more than the helium data line which stops losing weight at about 600 C. The third weight loss of 10 to 15 wt% is probably due to the reaction of hydrogen with the remaining carbon to produce $CH_4$ and other hydrocarbons. Similar results are shown in Figure I-5 for Fir wood. These PTGA results are in accord with our tubular reactor expeimental results.

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Data Tables I-2 and I-3 show the results of measurements that were obtained for conditions when the biomass is gradually fed into the reactor by the feeder. The reactor was heated up to 800 C before the start of the expeimental run, and the system is filled with hydrogen to pressures of 32.0 and 52.4 atm respectively. Data Table I-3 showing the results of Run No. 1152 gives the measurements obtained at 800 C and 52.4 atm initial pressure of hydrogen, whereas Data Table I-2 of Run No. 1144 was obtained at 800 C and an initial pressure of 32.0 atm. Table I-2 shows the initial conditions of the experiments for the two runs reffered to in Data Tables I-2 and I-3, respectively.

**TABLE I-2.** INITIAL CONDITION FOR THE EXPERIMENTAL RUNS

| Exp. No. | Temperature C | Initial Pressure atm | Biomass* Feed Rate grams/min. | Biomass* Quantity grams |
|---|---|---|---|---|
| Data Table I-2 Run No. 1144 | 800 | 32.0 | 16.9 | 184 |
| Data Table I-3 Run No. 1152 | 800 | 52.4 | 10.1 | 152 |

*The biomass used in both runs includes 20 wt% Silica

The biomass feeding times are 11 min. for Data Table I-2 and 12 min. for Data Table I-3. The total conversion of biomass to generated gases in these two runs are 88.5 wt% and 89.6 wt% respectively, based on the remaining char in the reactor at the end of the runs. These results confirm the earlier dilute phase, short residence time flash hydropyrolysis[I-2,I-3] where over 90 % conversions were obtained at 800 to 1000 C and 35.0 atm pressure.

The change in the number of moles of gas in the reactor during the run has been calculated from the pressure change and is graphically given in Figure I-6 and I-8. The calculated data include the net molar change of both the generated gases, CO, $CO_2$, and $CH_4$ and the hydrogen gas consumed. These calculated data do not accurately indicate the change of the total moles in the gas phase, because water ($H_2O$) formed in the gases was not measured. However the

data give some indication of the rate of the reaction. The slope of the change in numbers of moles in the reactor shown in Figure I-6, increases with time more slowly than that shown in Figure I-8. The reaction appears to continue for 30 min. of residence time, which is almost 20 min. after all of the biomass was fed into the reactor. On the other hand, under the condition of 52.4 atm of initial hydrogen atmosphere in Figure I-8, it appears to stop at around 15 min, only 3 min. after completion of feeding the biomass. These results indicate that the hydrogasification is favored by higher hydrogen pressure.

Table I-3 below shows the initial rate of molar change. These data were calculated by taking into account the initial molar change data in each run and dividing by the feed rate of the biomass.

TABLE I-3. INITIAL RATE OF MOLAR CHANGE
IN THE HYDROPYROLYSIS OF WOOD

| Exp. No. | Molar Change Rate mol/min.gram-biomass |
|---|---|
| Data Table I-2 800 C 32.0 atm | 0.012 |
| Data Table I-3 800 C 52.4 atm | 0.036 |

The initial rate of molar numbers change of Data Table I-3 is 3 times as large as that of Data Table I-2, even though the biomass used was smaller than in Data Table I-2. This result also implies that the total pressure of gaseous hydrogen strongly affects the rate of the reaction of biomass.

The gaseous concentrations shown in Data Table I-3 are also higher than those of Data Table I-2; $CH_4$ concentrations in Data Table I-3 are in the range between 25 and 30 vol%, whereas those in Data Table I-2 are 16 to 20 vol%. As indicated previously, the amount of biomass fed into the reactor in Data Table I-3 is smaller than in Data Table I-2. These results indicate that the higher pressure is more effective in promoting gasification and hydrogasification of biomass.

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In both Data Tables I-2 and I-3, the average ratio of the gases generated, CO, $CO_2$, and $CH_4$ are appro:    ^tely 3 : 1 : 3. Taking this ratio, and unreacted carbon of 10 to 15 wt%, into account and pe    .rming C, H and O mass balances, the following stoichiometric overall equation for hydropyrolysis of biomass at 800 C is derived.

$$CH_{1.44}O_{0.5} \xrightarrow[\text{heat}]{\text{hydrogen}} 0.3CO + 0.1\,CO_2 + 0.3CH_4 + 0.3C + 0.12H_2$$
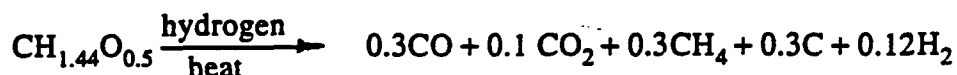
This eqr:~tion indicates that hydrogen is generated from the biomass. However, hydrogen is necessary to enhance the formation of $CH_4$. Taking the sum of the molar number, 0.82 mol/mol-biomass, of gas generated in this equation and the initial rate of molar change cited earlier into account, the initial rate of biomass conversion to gases is determined in Table I-4.

TABLE I-4.  INITIAL RATE OF THE BIOMASS CONVERSION

| Exp. No. | Initial Rate of Biomass to Gas (1 / min.) |
|---|---|
| Data Table I-2 800 C 32.0 atm | 0.31 |
| Data Table I-3 800 C 52.4 atm | 0.92 |

According to the result of the initial rate from Data Table I-3 at 800 C and 52.4 atm, approximately 92 wt% of the biomass appears to be converted to gases in one minute. For the conditions of Data Table I-2 at 800 C and 32.0 atm, a 31 % per min. conversion rate is obtained. The fact that an increase in pressure by a factor of 2 results in an increase in rate by a factor of 3, indicates the very strong effect of pressure on the rate.

It should be noted that a number of additional runs were made during the course of this work, but the data could not be accurately presented because of operational leaks of gases from the system during the runs.

## CONCLUSIONS

The following conclusions are derived from this work.

(1) Biomass hydropyrolysis conversion of 88 through 90 wt% can be obtained at temperature up to 800 C and initial hydrogen pressure of 32.0 and 52.4 atm respectively.

(2) The initial rate of biomass conversion of 0.31 1/min. is obtained at an initial pressure of 32.0 atm and 800 C, and a higher value of 0.92 1/min. is obtained at the higher pressure of 52.4 atm and 800 C. Hydrogen pressure has a significant enhancing effect on the rate of conversion of biomass to gases.

(3) Higher temperatures, above 700 C, and rapid heat-up rate enhance the conversion of biomass to $CH_4$ and CO.

(4) At low heat-up rate the reaction appears to proceed in two steps: pyrolysis at 300 to 400 C followed by hydropyrolysis at temperatures up to 700 C or higher.

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I-2. M. Steinberg and P. Fallon: "Flash Pyrolysis and Hydropyrolysis of Biomass," BNL 30263, Brookhaven National Laboratory, Upton, NY (October 1981)

I-3. M. S. Sundram, M. Steinberg, and P. T. Fallon; "Characterization of the Products and Comparison of the Product Yields from the Flash Pyrolysis of Fir Wood in Hydrogen and Helium," Symposium paper of Energy from Biomass and Wastes 8th, pp 1395-1416(1984)

I-4. R. Khan, Private Communication (August 19, 1991)

TABLE I-5. EXPERIMENTAL DATA FOR THE HYDROGASIFICATION
OF BIOMASS

```
Hydropyrolysis of biomass        Run No. 1154
November 26,1991      14: 30 - 17: 00
Preloaded biomass is heated up in the closed system
Wood  130   gram  preloaded  including SiO2   26 grams
Alumina balls 50 grams
Hydrogen feed rate    0    m3/min.
Temperature    - 800 degree centigrade
Pressure          52.4-  atm
```

| Time min. | Press atm | Reactor Temperature C | Concentrations of Generated gases | | | Vol% |
| | | | CO | CO2 | CH4 | C2H6 |
|---|---|---|---|---|---|---|
| 0 | 52.4 | 35 | | | | |
| 1 | 52.4 | 46 | | | | |
| 6 | 52.4 | 118 | | | | |
| 11 | 53.0 | 212 | | | | |
| 16 | 53.5 | 305 | | | | |
| 20 | 54.4 | 375 | | | | |
| 21 | 55.7 | 383 | | | | |
| 24 | 55.6 | 432 | | | | |
| 26 | 55.6 | 452 | | | | |
| 31 | 55.6 | 504 | | | | |
| 33 | | | 5.2 | 8.9 | 0.4 | |
| 38 | 55.7 | 575 | | | | |
| 41 | 55.7 | 595 | 9.7 | 21.3 | 0.9 | |
| 46 | 55.7 | 628 | 11.0 | 23.3 | 1.5 | |
| 51 | 55.7 | 652 | | | | |
| 54 | | | 11.6 | 23.0 | 3.5 | 0.4 |
| 56 | 55.6 | 681 | | | | |
| 61 | 55.7 | 718 | | | | |
| 66 | 55.7 | 729 | | | | |
| 71 | 55.6 | 750 | 7.8 | 21.7 | 12.1 | 1.8 |
| 76 | 55.6 | 768 | 7.0 | 24.3 | 18.8 | 2.8 |
| 81 | 55.6 | 783 | | | | |
| 86 | 55.6 | 800 | | | | |
| 91 | 55.6 | 813 | | | | |
| 96 | 55.6 | 813 | | | | |
| 101 | 55.6 | 814 | | | | |
| 106 | 55.6 | 814 | 5.6 | 29.4 | 25.7 | 3.4 |
| 111 | 55.6 | 814 | | | | |
| 123 | 55.4 | 813 | | | | |
| 135 | 55.3 | 813 | | | | |

```
Residue in the reactor and char trap
        63  grams including 26 grams Silica

Some water ( about 5 cc ) remained in the char trap
and inside reactor.
```

## TABLE I-6. EXPERIMENTAL DATA FOR THE HYDROGASIFICATION IN THE RAPID HEATING UP OF THE BIOMASS.

### AT 800 C AND AT 32.0 atm OF INITIAL HYDROGEN PRESSURE

Hydrocarb Process Test for Biomass
Run Number 1144
October 21,1991
Wood 184.8grm       Wood content 80 %    SiO2 content 20 %
                    147.8 grms           36.96 grms
800 C  32.0 atm    Biomass Feed Rate 16.9 grms/min.
Residue 54 grms including SiO2  Biomass Conversion 88.5 wt%

| time | CO Vol% | CO2 Vol% | CH4 Vol% | Press psig | Press atm | Molar Change dn/dt mol/min | Total mol |
|---|---|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 455 r | 31.95 | 0.0000 | 0.0000 |
| 1 | | | | 462.5 ave | 32.46 | 0.2448 | 0.2448 |
| 2 | 19.7 | 7.1 | 20.1 | 470 r | 32.97 | 0.2448 | 0.4896 |
| 3 | | | | 478 r | 33.52 | 0.2611 | 0.7507 |
| 4 | | | | 476.5 ave | 33.41 | -0.0490 | 0.7017 |
| 5 | 16.4 | 8.9 | 16.8 | 475 r | 33.31 | -0.0490 | 0.6528 |
| 6 | | | | 478.5 ave | 33.55 | 0.1142 | 0.7670 |
| 7 | | | | 482 r | 33.79 | 0.1142 | 0.8813 |
| 8 | | | | 486 r | 34.06 | 0.1306 | 1.0118 |
| 9 | | | | 486 r | 34.06 | 0.0000 | 1.0118 |
| 10 | | | | 488 ave | 34.2 | 0.0653 | 1.0771 |
| 11 | 16 | 6 | 16 | 490 r | 34.33 | 0.0653 | 1.1424 |
| 12 | | | | 491 ave | 34.4 | 0.0326 | 1.1750 |
| 13 | | | | 492 r | 34.47 | 0.0326 | 1.2077 |
| 14 | | | | 497.5 ave | 34.84 | 0.1795 | 1.3872 |
| 15 | 16.2 | 4.4 | 17.5 | 503 r | 35.22 | 0.1795 | 1.5667 |
| 16 | | | | 506 ave | 35.42 | 0.0979 | 1.6646 |
| 17 | | | | 509 ave | 35.63 | 0.0979 | 1.7625 |
| 18 | 18.5 | 7.2 | 18.8 | 512 r | 35.83 | 0.0979 | 1.8604 |
| 19 | | | | 514 ave | 35.97 | 0.0653 | 1.9257 |
| 20 | | | | 516 r | 36.1 | 0.0653 | 1.9910 |
| 21 | | | | 519 ave | 36.31 | 0.0979 | 2.0889 |
| 22 | | | | 522 r | 36.51 | 0.0979 | 2.1868 |
| 23 | | | | 526 ave | 36.78 | 0.1306 | 2.3174 |
| 24 | | | | 530 r | 37.05 | 0.1306 | 2.4480 |
| 25 | | | | 532 ave | 37.19 | 0.0653 | 2.5132 |
| 26 | | | | 534 r | 37.33 | 0.0653 | 2.5785 |
| 27 | | | | 536 ave | 37.46 | 0.0653 | 2.6438 |
| 28 | | | | 538 ave | 37.6 | 0.0653 | 2.7091 |
| 29 | 24 | 7.7 | 26.8 | 540 r | 37.73 | 0.0653 | 2.7744 |
| 30 | | | | 541 ave | 37.8 | 0.0326 | 2.8070 |
| 31 | | | | 542 r | 37.87 | 0.0326 | 2.8396 |
| 32 | | | | 542 ave | 37.87 | 0.0000 | 2.8396 |
| 33 | | | | 542 r | 37.87 | -0.0000 | 2.8396 |
| 34 | | | | 540 ave | 37.73 | -0.0653 | 2.7744 |
| 35 | 16.4 | 5.1 | 18.6 | 538 r | 37.6 | -0.0653 | 2.7091 |
| 36 | | | | 536.5 ave | 37.5 | -0.0490 | 2.6601 |
| 37 | | | | 535 ave | 37.39 | -0.0490 | 2.6112 |
| 38 | | | | 533.5 ave | 37.29 | -0.0490 | 2.5622 |
| 39 | | | | 532 r | 37.19 | -0.0490 | 2.5132 |
| 40 | | | | 531.4 ave | 37.15 | -0.0196 | 2.4937 |
| 41 | | | | 530.8 ave | 37.11 | -0.0196 | 2.4741 |
| 42 | | | | 530.2 ave | 37.07 | -0.0196 | 2.4545 |
| 43 | | | | 529.6 ave | 37.03 | -0.0196 | 2.4349 |
| 44 | | | | 529 r | 36.99 | -0.0196 | 2.4153 |
| 45 | | | | 528.2 ave | 36.93 | -0.0261 | 2.3892 |
| 46 | | | | 527.4 ave | 36.88 | -0.0261 | 2.3631 |
| 47 | | | | 526.6 ave | 36.82 | -0.0261 | 2.3370 |
| 48 | | | | 525.8 ave | 36.77 | -0.0261 | 2.3109 |
| 49 | | | | 525 r | 36.71 | -0.0261 | 2.2848 |
| 50 | | | | 522.8 ave | 36.57 | -0.0707 | 2.2140 |
| 51 | | | | 520.7 ave | 36.42 | -0.0707 | 2.1433 |
| 52 | | | | 518.5 ave | 36.27 | -0.0707 | 2.0726 |
| 53 | | | | 516.3 ave | 36.12 | -0.0707 | 2.0019 |
| 54 | | | | 514.2 ave | 35.98 | -0.0707 | 1.9312 |
| 55 | | | | 512 r | 35.83 | -0.0707 | 1.8604 |
| 56 | | | | 500.7 ave | 35.06 | -0.3699 | 1.4905 |
| 57 | | | | 489.3 ave | 34.29 | -0.3699 | 1.1206 |
| 58 | | | | 478 r | 33.52 | -0.3699 | 0.7507 |

# TABLE I-7. EXPERIMENTAL DATA FOR THE HYDROGASIFICATION IN THE RAPID HEATING UP OF THE BIOMASS.

## AT 800 C AND AT 52.4 atm OF INITIAL HYDROGEN PRESSURE

Hydrocarb Process Test for Biomass
Run number 1152
November 18,1991
Wood 152 grms      Wood content 80 % and SiO2 20 %
                     121.6 grms      30.4 grms
800 C   52.4 atm       Wood Feed Rate       10.1 grms/min.
Residue     43grms including SiO2   Biomass Conversion 89.6wt%

| | Generated Gases | | | | | Molar Change | Total |
|---|---|---|---|---|---|---|---|
| time | CO Volt | CO2 Volt | CH4 Volt | Press psig | Press atm | dn/dt mol/min | mol |
| 0 | 0 | 0 | 0 | 755 | 52.36 | 0.0000 | 0.0000 |
| 1 | | | | 769 | 53.31 | 0.4570 | 0.4570 |
| 2 | | | | 776 | 53.79 | 0.2285 | 0.6855 |
| 3 | | | | 779 | 53.99 | 0.0979 | 0.7834 |
| 4 | | | | 780 | 54.06 | 0.0326 | 0.8160 |
| 5 | | | | 783 | 54.27 | 0.0979 | 0.9139 |
| 6 | | | | 784 | 54.33 | 0.0326 | 0.9466 |
| 7 | | | | 786 | 54.47 | 0.0653 | 1.0119 |
| 8 | | | | 788 | 54.61 | 0.0653 | 1.0771 |
| 9 | | | | 791.5 | 54.84 | 0.1142 | 1.1914 |
| 10 | | | | 795 | 55.08 | 0.1142 | 1.3056 |
| 11 | | | | 800 | 55.42 | 0.1632 | 1.4688 |
| 12 | | | | 804 | 55.69 | 0.1306 | 1.5994 |
| 13 | | | | 807 | 55.90 | 0.0979 | 1.6973 |
| 14 | — | | | 809 | 56.03 | 0.0653 | 1.7626 |
| 15 | | | | 811 | 56.17 | 0.0653 | 1.8279 |
| 16 | | | | 812 | 56.24 | 0.0326 | 1.8605 |
| 17 | | | | 811.5 | 56.20 | -0.0163 | 1.8442 |
| 18 | | | | 811 | 56.17 | -0.0163 | 1.8279 |
| 19 | | | | 810.5 | 56.14 | -0.0163 | 1.8116 |
| 20 | | | | 810 | 56.10 | -0.0163 | 1.7952 |
| 21 | | | | 809.5 | 56.07 | -0.0163 | 1.7789 |
| 22 | | | | 809 | 56.03 | -0.0163 | 1.7626 |
| 23 | | | | 808.5 | 56.00 | -0.0163 | 1.7463 |
| 24 | 33.4 | 14.7 | 29.5 | 808 | 55.97 | -0.0163 | 1.7300 |
| 25 | | | | 807.5 | 55.93 | -0.0163 | 1.7136 |
| 26 | | | | 807 | 55.90 | -0.0163 | 1.6973 |
| 27 | | | | 806.5 | 55.86 | -0.0163 | 1.6810 |
| 28 | | | | 806 | 55.83 | -0.0163 | 1.6647 |
| 29 | | | | 806 | 55.83 | 0.0000 | 1.6647 |
| 30 | | | | 806 | 55.83 | 0.0000 | 1.6647 |
| 31 | | | | 806 | 55.83 | 0.0000 | 1.6647 |
| 32 | | | | 806 | 55.83 | 0.0000 | 1.6647 |
| 33 | | | | 806.5 | 55.86 | 0.0163 | 1.6810 |
| 34 | 26 | 8.4 | 24.9 | 807 | 55.90 | 0.0163 | 1.6973 |
| 35 | | | | 806.75 | 55.88 | -0.0082 | 1.6892 |
| 36 | | | | 806.5 | 55.86 | -0.0082 | 1.6810 |
| 37 | | | | 806.25 | 55.85 | -0.0082 | 1.6728 |
| 38 | 25.7 | 8.1 | 28.6 | 806 | 55.83 | -0.0082 | 1.6647 |
| 39 | | | | 805.33 | 55.78 | -0.0218 | 1.6429 |
| 40 | | | | 804.67 | 55.74 | -0.0218 | 1.6212 |
| 41 | | | | 804 | 55.69 | -0.0218 | 1.5994 |
| 42 | | | | 804.25 | 55.71 | 0.0082 | 1.6076 |
| 43 | | | | 804.5 | 55.73 | 0.0082 | 1.6157 |
| 44 | | | | 804.75 | 55.74 | 0.0082 | 1.6239 |
| 45 | | | | 805 | 55.76 | 0.0082 | 1.6320 |
| 46 | | | | 805 | 55.76 | 0.0000 | 1.6320 |
| 47 | | | | 805 | 55.76 | 0.0000 | 1.6320 |
| 48 | | | | 805 | 55.76 | 0.0000 | 1.6320 |
| 49 | | | | 804.67 | 55.74 | -0.0109 | 1.6212 |
| 50 | | | | 804.33 | 55.72 | -0.0109 | 1.6103 |
| 51 | | | | 804 | 55.69 | -0.0109 | 1.5994 |
| 52 | | | | 804.5 | 55.73 | 0.0163 | 1.6157 |
| 53 | | | | 805 | 55.76 | 0.0163 | 1.6320 |
| 54 | | | | 804.8 | 55.75 | -0.0065 | 1.6255 |
| 55 | | | | 804.6 | 55.73 | -0.0065 | 1.6190 |
| 56 | | | | 804.4 | 55.72 | -0.0065 | 1.6125 |
| 57 | | | | 804.2 | 55.71 | -0.0065 | 1.6059 |
| 58 | | | | 804 | 55.69 | -0.0065 | 1.5994 |
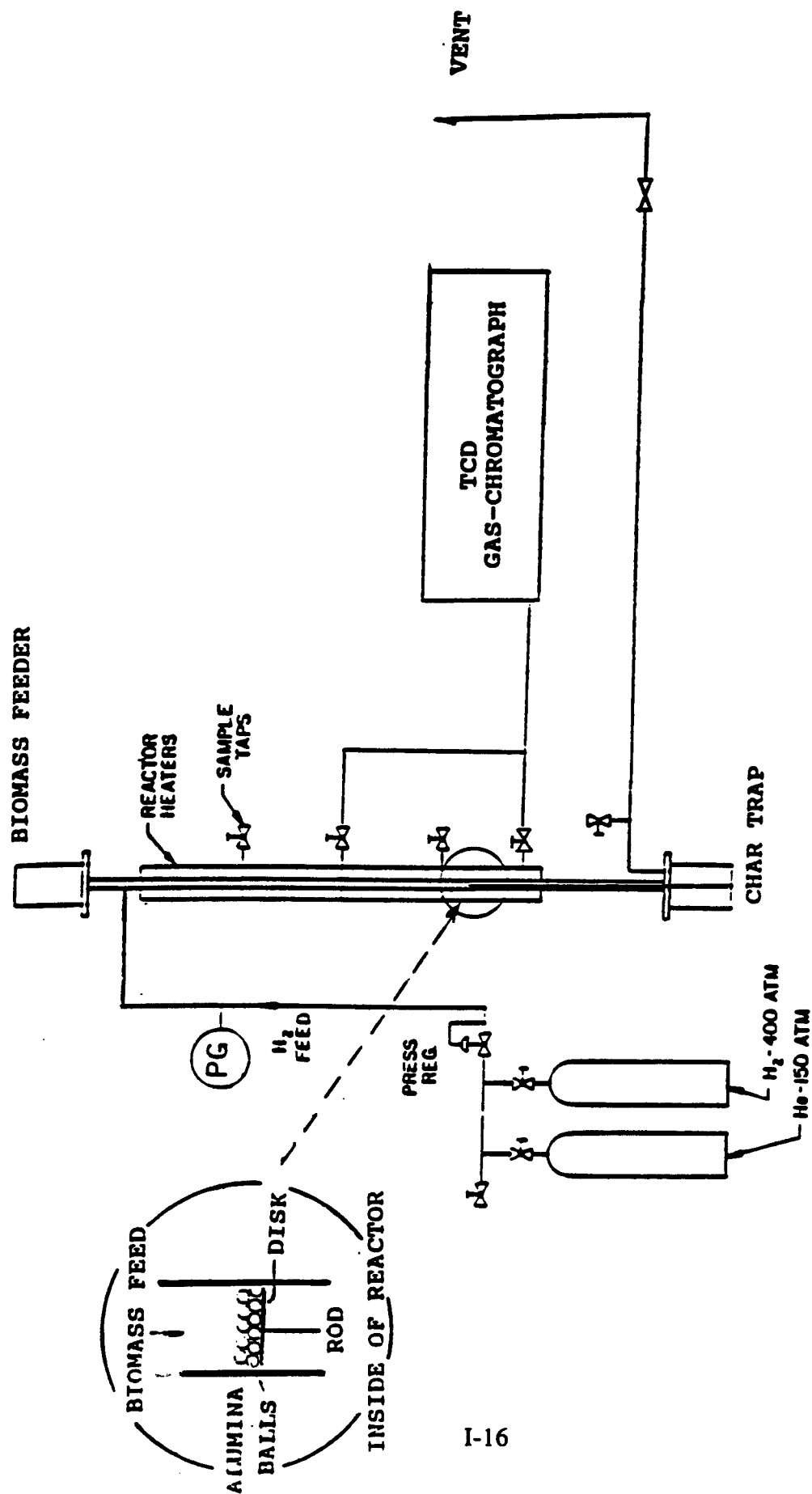
FIGURE I-1. Schematic Flow Sheet of Tubular Reactor Equipment.

I-16
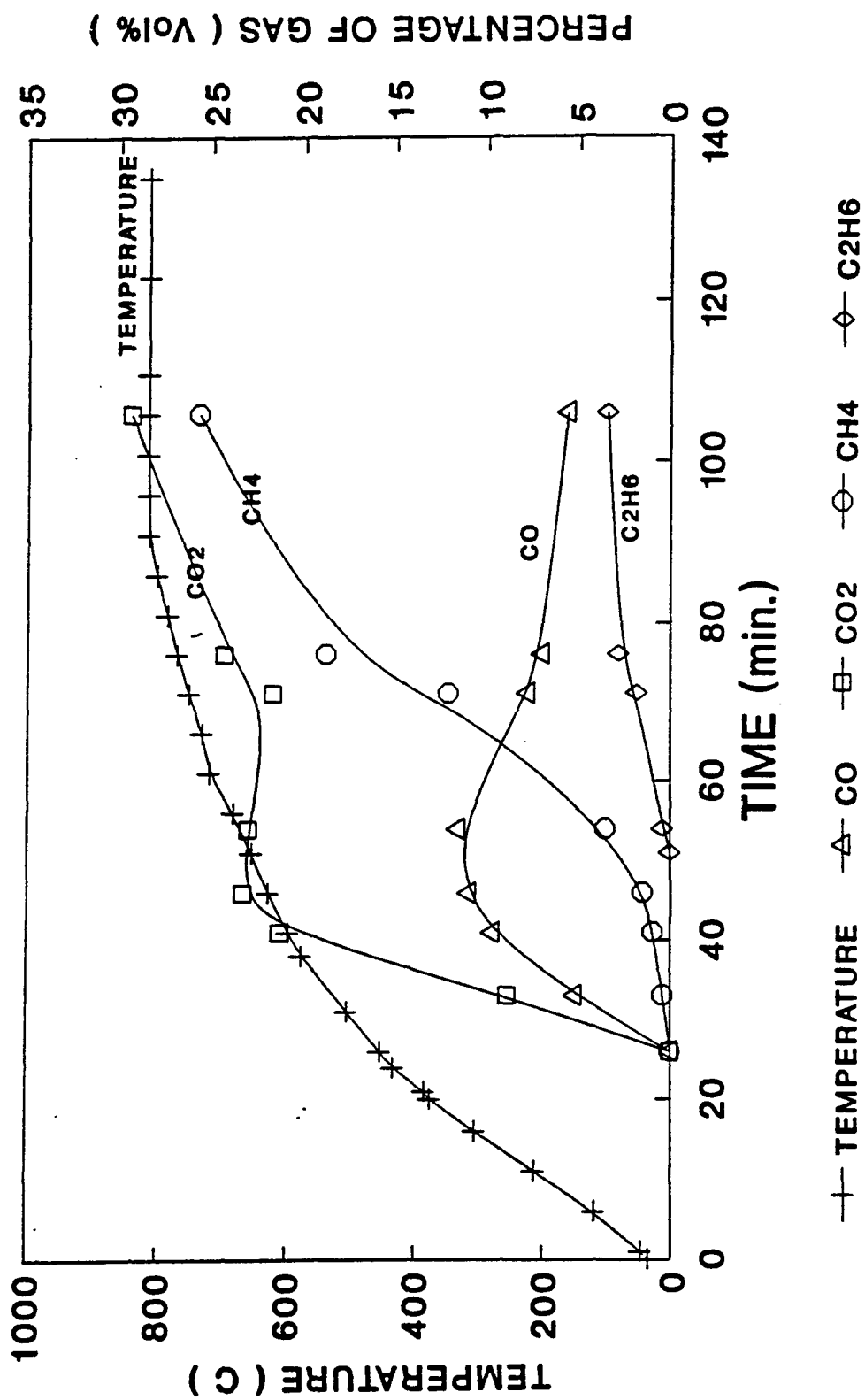
FIGURE I-2. Reactor Temperature, Generated Gases, vs. Lapse of Time at 52.4 atm, 100% hydrogen of the beginning pressure

I-17
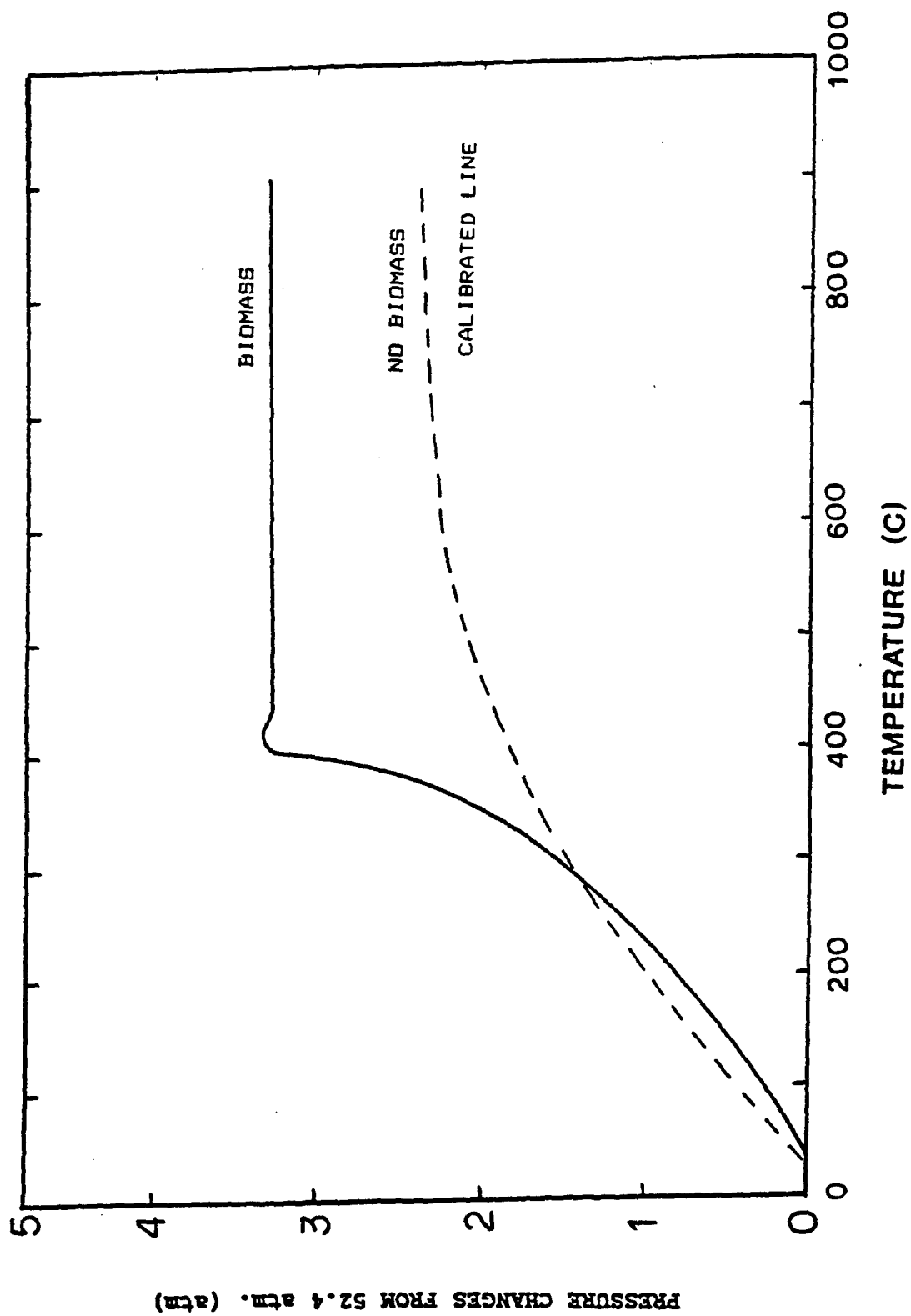
FIGURE I-3. Pressure Change in Reactor vs. Reactor Temperature.
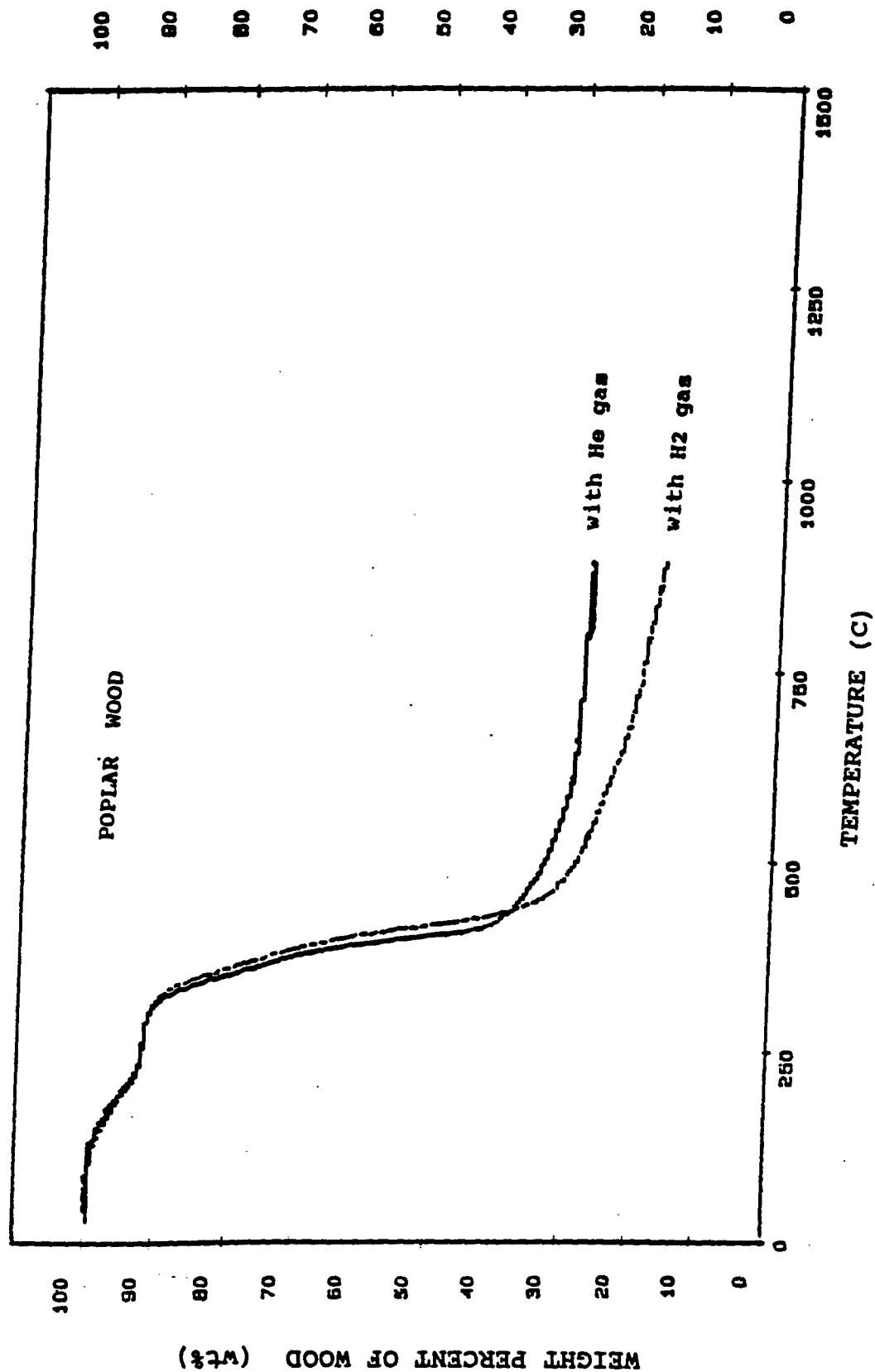
FIGURE I-4. Weight Losing Curve of Biomass (Popular Wood) with Temperature using PTGA (Pressurized Thermogravimetric Analyzer) at Heat-up Rate of 50 C/min. and 28.2 atm.

I-19
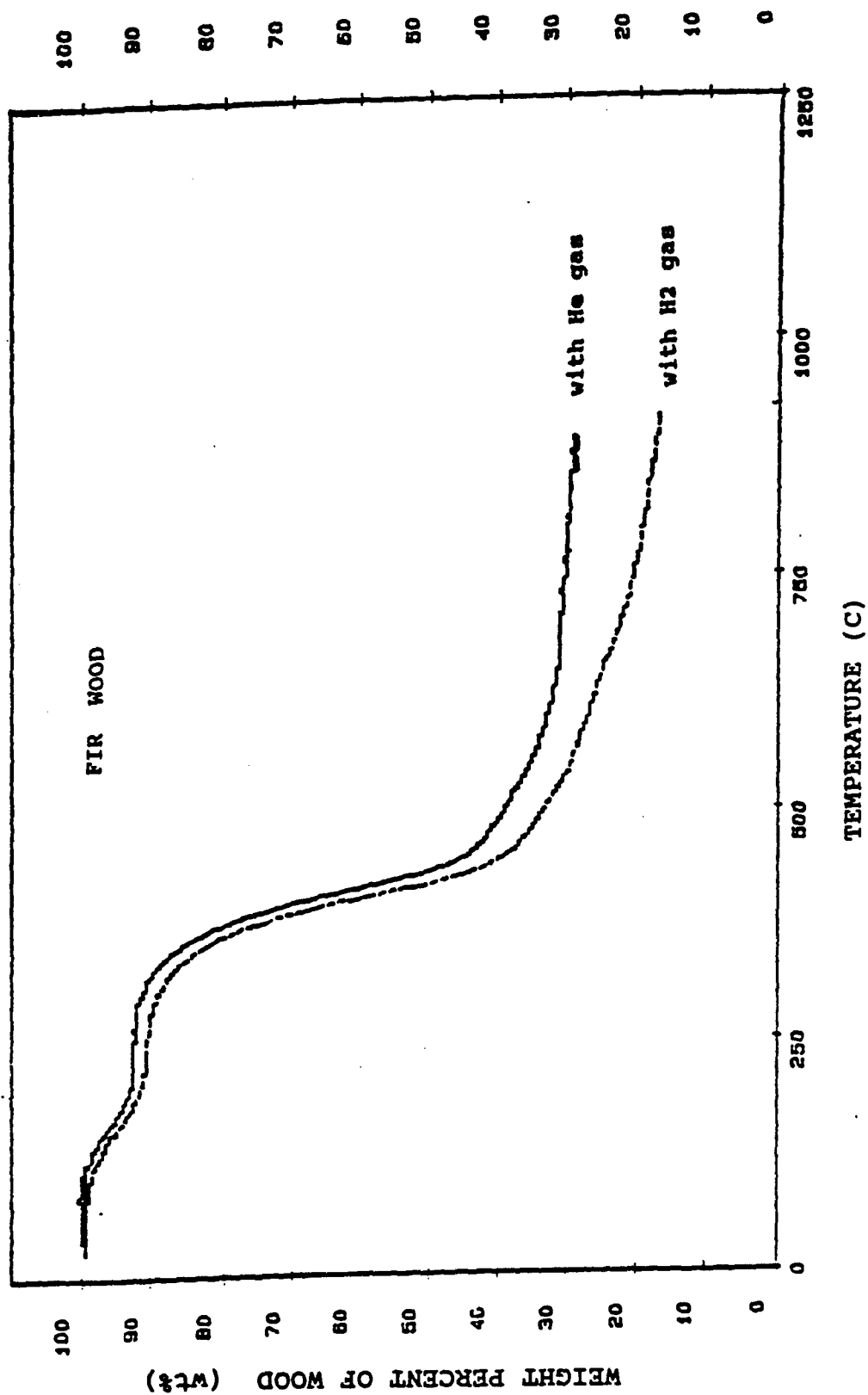
FIGURE I-5. Weight Losing Curve of Biomass (Fir Wood) with Temperature using PTGA (Pressurized Thermogravimetric Analyzer) at Heat-up Rate of 50 C/min. and 28.2 atm.
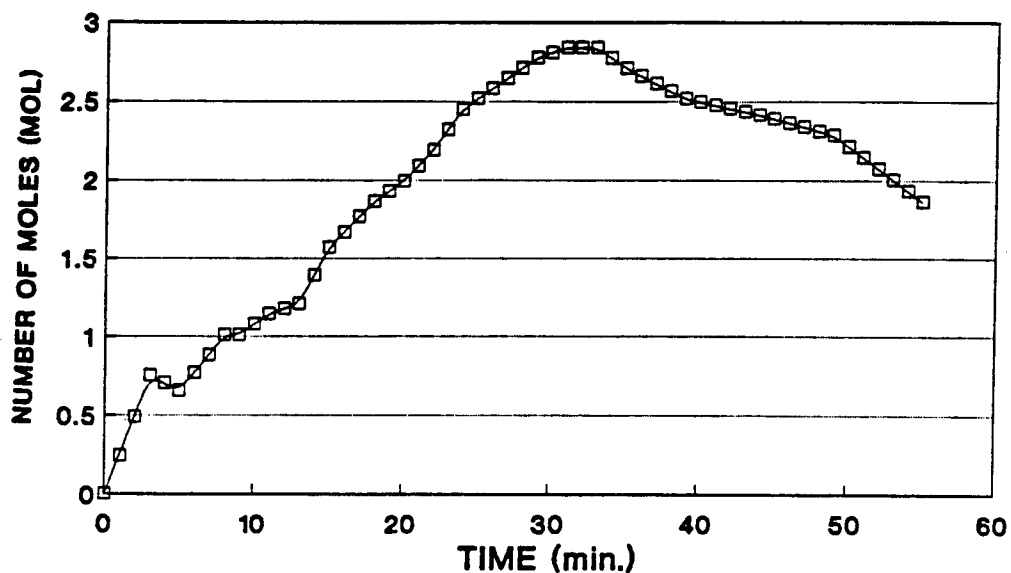
Figure I-6. The Change in Number of Moles in the Reactor with Time at 800 C and 32.0 atm of
Initial Hydrogen Pressure.

Run No. 1144 – Data Table I-2
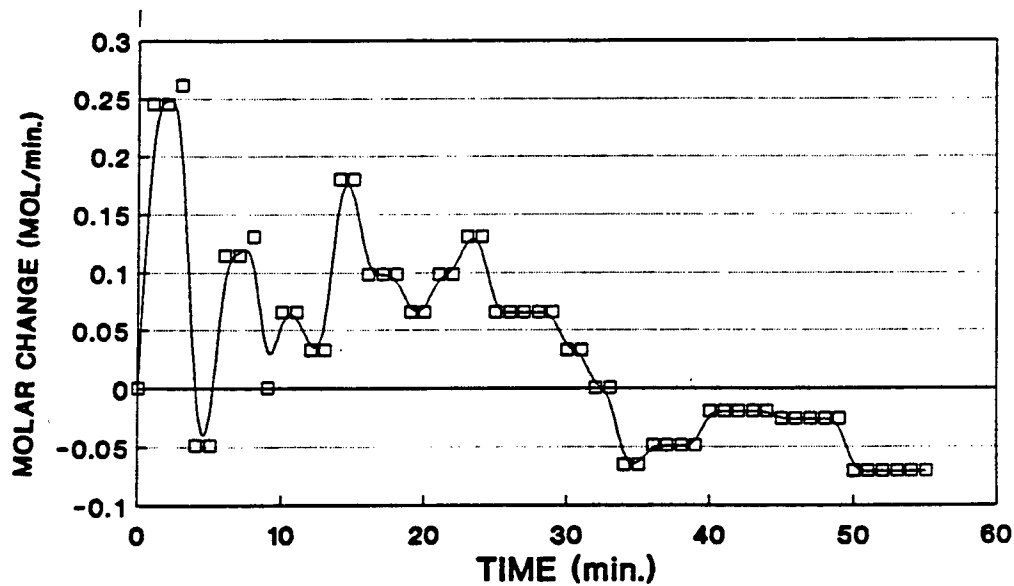


Figure I-7. The Rate of Molar Change with Time at 800 C and 32.0 atm of Initial Hydrogen
Pressure.

Run No. 1144 – Data Table I-2

I-21
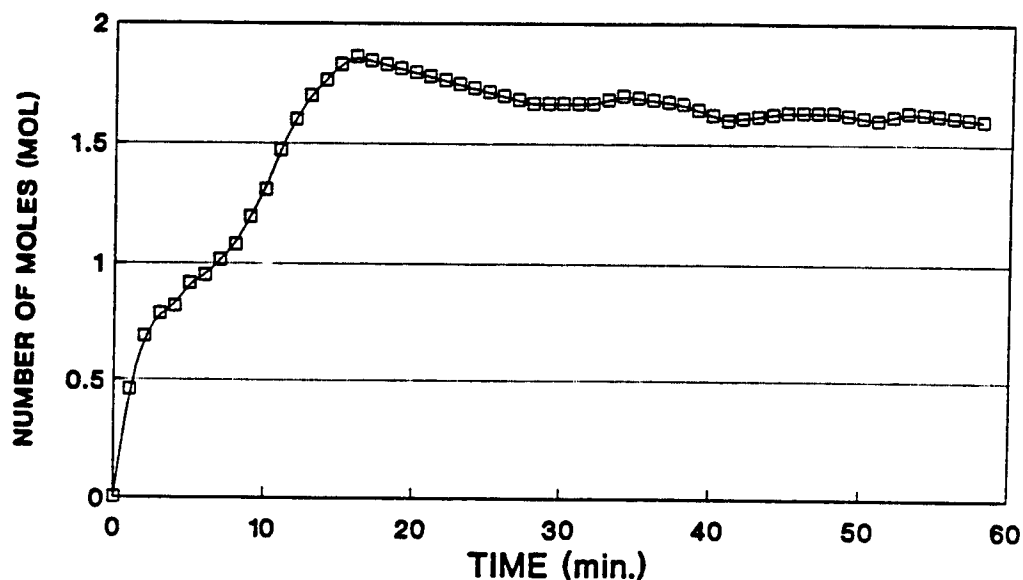
Figure I-8. The Change in Number of Moles in the Reactor with Time at 800 C and 52.4 atm of Initial Hydrogen Pressure.

Run No. 1152 – Data Table I-7
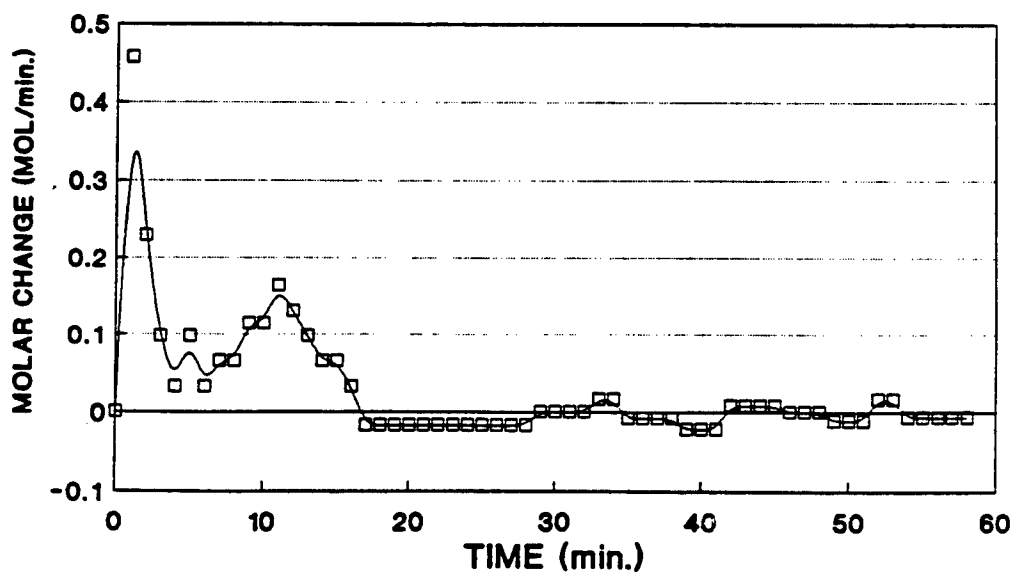


Figure I-9. The Rate of Molar Change with Time at 800 C and 52.4 atm of Initial Hydrogen Pressure.

Run No. 1152 – Data Table I-7

I-22

**Part II**


# THE THERMAL DECOMPOSITION OF METHANE IN A TUBULAR REACTOR

ATSUSHI KOBAYASHI AND MEYER STEINBERG


BROOKHAVEN NATIONAL LABORATORY
Upton, Long Island, NY, 11973

# The Thermal Decomposition of Methane in a Pressurized Tubular Reactor

by

Atsushi Kobayashi and Meyer Steinberg

Brookhaven National Laboratory

Upton, New York, 11973

## ABSTRACT

The reaction rate of methane decomposition using a tubular reactor having a 25.4 mm inside diameter with a 2.44 m long heated zone was investigated in the temperature range of 700 to 900 C with pressures ranging from 28.2 to 56.1 atm. Representing the rate by a conventional model, $-dC_{CH4}/dt = k1\ C_{CH4} - k2\ C_{H2}^2$, the rate constant k1 for methane decomposition was determined. The activation energy, 31.3 kcal/mol, calculated by an Arrhenius Plot was lower than for previously published results for methane decomposition. This result indicates that submicron particles found in the reactor adhere to the inside of the reactor and these submicron high surface area carbon particles tend to catalyze the methane decomposition. The rate constant has been found to be approximately constant at 900 C with pressure range cited above. The rate of methane decomposition is first-order with respect to methane partial pressure. The rate of the methane decomposition is favored by higher temperatures and pressures while the thermochemical equilibrium of methane decomposition is favored by lower pressures.

# INTRODUCTION

The Hydrocarb Process[II-1] consists of the two main reactions; (1) hydrogasification of the carboneous feedstock to produce a methane-rich gas and (2) the thermal decomposition of methane to produce carbon black and a hydrogen-rich gas. The section on methane decomposition is especially important in order to maintain high efficiency in the process. A key element in the process is that the hydrogen-rich gas produced in the methane decomposition reactor is recycled to the hydrogasification reactor as the reactant gas. Furthermore, the product carbon black is produced in the methane decomposition section.

This work was performed in order to investigate the phenomena of methane decomposition and to obtain data on the kinetics of the reaction for the purpose of designing the methane decomposition reactor.

# CHEMICAL EQUILIBRIUM

Since the met. decomposition is endothermic, the methane concentration decreases with increasing ter ature. Due to the increase of volume during methane decomposition, the decomposition of methane is favored by decreasing pressure.

$$CH_4 = C + 2 H_2 - 17.9 \text{ kcal/mol} \tag{1}$$
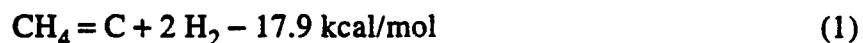
Figure II-1 shows the equilibrium data of the methane at temperature from 600 to 1200 C and at pressures of 25, 30, 40, and 50 atm. These data are calculated from the following Gibbs Free Energy and equilibrium constant.

$$R T \ln K_x = -dG \tag{2}$$

$$K_x = X_{H2}^2 / X_{CH4} \tag{3}$$

where X is the mol fraction of each gaseous component, and

$$K_p = \left(P_{H2}\right)^2 / P_{CH4} \tag{4}$$

where pp is the partial pressure of each component

# EXPERIMENTAL DESCRIPTION

Figure II-2 shows the schematic flow sheet of the experimental equipment which mainly consists of a tubular reactor, a carbon trap, a gas-chromatograph and gas meter. Methane enters the system through a remotely controlled regulator located next to the methane cylinders which keeps the pressure approximately constant at selected pressure of 28.2, 41.8 or 56.1 atm in the system. Methane then flows through a preheater and enters the reactor which consists of a 25.4 mm inside diameter by 6.35 mm wall Inconel 617 tube. The total length of the reactor tube is 3.35 m of which the first 2.44 m is externally heated and selectively maintained at constant experimental temperatures of 700, 800 and 900 C by clamshell electric heaters. Methane is decomposed into carbon and hydrogen in the heated reactor and the effluent gas flows through the carbon trap connected at the bottom of the reactor, where the carbon generated by the reaction is separated. Gas is sampled before and after the reactor and analyzed by an on-line gas-chromatograph which measures the concentrations of $CH_4$, CO, and $CO_2$ in the gas by a thermal conductivity detector. The flow rate of exit gas is controlled in the range between 10 and 150 liters/min. by a flow valve located after the reactor. The exit gas flows through the gas meter where the flow rate is measured and the gas is finally vented to the atmosphere.

## EXPERIMENTAL RESULT AND DISCUSSION

Table II-1 shows the results of the data for the experimental runs to measure the conversion of methane into hydrogen and carbon at 700, 800, and 900 C and at 56.1, 41.8 and 28.2 atm. Figure II-3 shows the relationship between the methane concentrations in exit gas and residence time in the reactor under these conditions. The residence time of the methane gas in the reactor is given by the inlet gas velocity. The concentration of the methane decreases with increasing temperature and residence time. At both 700 and 800 C and at 56.1 atm the concentration of methane decreases less with residence time than that at 900 C and 56.1 atm. Under the latter conditions, the concentration of methane decreases dramatically with residence time and appears to be approaching equilibrium conditions. The concentration of methane at a residence time of 103 seconds was 48.1 vol%, and in this case the equilibrium concentration of the methane is 39.6 vol%.

The equilibrium data at the lower temperatures of 700 and 800 C and at 56.1 atm are 54.3 and 69.3 vol% respectively and higher than that at 900 C. Taking these conditions into account and considering the curves of methane decomposition in Figure II-3, the rate of methane decomposition in the lower temperature range seems to be much smaller than that at the higher temperature of 900 C.

Generally the equation for the rate of decomposition of methane is derived as follows;

$$CH_4 \underset{k2}{\overset{k1}{\rightleftharpoons}} C + 2H_2 \tag{5}$$

where k1 is the rate constant of methane decomposition, and k2 is the rate constant of methane formation.

The rate equation for this reversible reaction can be written as follows;

$$-r_{CH4} = -dC_{CH4} / dt = k1\, C_{CH4} - k2\, C_{H2}^2$$

$$= k1\, C_{CH4} \left( 1 - 1 / ke \times C_{H2^2} / C_{CH4} \right) \tag{6}$$

where $C_{CH4}$, $C_{H2}$ are the molar concentrations of CH4 and H2 respectively.

The above differential equation for methane decomposition in the tubular reactor is solved for the condition of $C_{H20} = 0$ (initial concentration of hydrogen is 0 ), for inlet methane concentration $C_{CH40}$, exit methane concentration $C_{CH4}$ and equilibrium concentration of methane $C_{CH4E}$. Figure II-4 shows a model of the tubular reactor and the derivation of the following rate equation.

$$k1 \times t = \frac{C_{CH40} - C_{CH4E}}{C_{CH40} + C_{CH4E}} \ln \frac{C^2_{CH40} - C_{CH4} \times C_{CH4E}}{C_{CH40} \times (C_{CH4} - C_{CH4E})} \tag{7}$$

where t is the residence time

Table II-2 shows the calculated data of inlet, outlet and equilibrium concentrations of methane, inlet flow rate, and $k1 \times t$ values. Figure II-5 shows the relationship between $k1 \times t$ value versus residence time at 700, 800, and 900 C and at 56.1 atm. Each slope in the Figure 5 indicates a rate constant $k1$ of the methane decomposition at each temperature. Table II-3 represents the $k1$ value at these conditions.

**TABLE II-3.** RATE CONSTANTS AT 56.1 ATM

| Temperature | k1 value | |
|---|---|---|
| 700  C | 5.758E-4 | 1/sec |
| 800  C | 1.753E-3 | 1/sec |
| 900  C | 9.306E-3 | 1/sec |

In Figure II-6, the rate constants, $k1$, for methane decomposition are plotted versus recipical temperature. From this Arrhenius plot an activation energy for methane decomposition and the rate constant $k1$ are calculated as follows;

$$E = 31.3 \text{ kcal/mol}$$

$$k1 = 5.4 \times 10^3 \exp(-E/RT) \qquad 1/sec \tag{8}$$

The activation energy appears to indicate a diffusion controlled process which usually has values up to about 30 kcal/mol as opposed to a chemical reaction controlled process which has much higher activation energies ranging above 50 kcal/mol. From the limited methane

decomposition data in the literatures,[II-2,3,4,5,and 6] the homogeneous activation energy for methane decomposition is determined to be 65 kcal/mol. The data gathered in these experiments appear to be influenced by a heterogeneous effect of surfaces. During our experiments some of the carbon formed from methane decomposition adhered to the walls of the Inconel high alloy steel of the tubular reactor. In fact, at the end of several extended runs, it was found that the carbon plugged the tube to the extent that it restricted the gas flow. Thus, the fine submicron carbon particles could tend to catalyze the thermal decomposition of the methane. References 7 and 8 clearly indicate that different materials increase the rate of the mathane decomposition in the order of iron oxide, alumina, graphite, and quartz. In the tubular reactor the small submicron particle size of the carbon presents a very large surface area on which methane can decompose and thus a lower activation energy for decomposition results.

The influence of the total pressure in this system on the rate constant of the methane decomposition was investigated because the Hydrocarb Process is being operated under pressure and it is important to determine the influence of the total pressure on the reaction rate. Figure II-7 shows the relationship between the $k1 \times t$ value and residence time at 28.2, 41.8, and 56.1 atm at 900 C. The slopes in Figure II-7 represent the rate constants $k1$ at their respective conditions. These values are calculated and listed in Table II-4.

TABLE II-4. RATE CONSTANTS AT 900 C

| Pressure | k1 value | |
|---|---|---|
| 28.2 atm | 1.066E-2 | 1/sec |
| 41.8 atm | 1.380E-2 | 1/sec |
| 56.1 atm | 9.036E-3 | 1/sec |

average rate constant 1.126E-2     1/sec

Although there is not enough data to establish a relationship with pressure, the rate constant appears to be really independent of pressure. The variation in the rate constant with pressure is probably within the deviation in the experimental measurements for this type of equipment.

Some other studies to obtain the rate data of carbon formation from methane on silicate substrate indicate that the rate increased in first-order with pressure up to 15 atm.[II-2] The rate equation (6) modelled in this paper indicates that since the methane molar concentration is first-order in pressure, the result that the rate constant is constant and independent of pressure is in accord with other published results; and the rate of the methane decomposition indeed increases with partial methane pressure approximately in first-order. The thermochemical equilibrium for methane decomposition is favored by lower pressures, but as our results indicate, the rate is favored by higher pressure.

## CONCLUSIONS

The influence of the temperature and total pressure on the rate of the methane decomposition has been determined by using a tubular reactor assembly. The following results and conclusions were obtained.

(1) A model for methane decomposition was developed, which resulted in the following rate equation;

$$-r_{CH4} = -dC_{CH4} / dt = k1\, C_{CH4} - k2\, C_{H2}^2$$

$$= k1\, C_{CH4} \left(1 - 1\,/\,ke \times C_{H2}^2\,/\,C_{CH4}\right)$$

k1 value was calculated as follows;

$$k1 \times t = \frac{C_{CH40} - C_{CH4E}}{C_{CH40} + CH4E} \ln \frac{C_{CH40}^2 - C_{CH4} \times C_{CH4E}}{C_{CH40} \times \left(C_{CH4} - C_{CH4E}\right)}$$

An Arrhenius Plot of the k1 values resulted in the following rate constant equation.

$$k1 = 5.4 \times 10^3 \exp\left(-31.3\ kcal/RT\right) \qquad 1/sec$$

The activation energy appears to indicate a diffusion controlled process most likely influenced by the high surface area of the submicron carbon particles deposited in the reaction zone.

(2) Although a definitive influence of the total pressure on the rate constant of the methane decomposition could not be clearly determined, at 900 C, within experimental error, the rate constant appears to be constant and independent of pressure in the range of 28.1 to 56.1 atm. Taking into account the rate equation modelled in this paper, the rate of decomposition is influenced by the methane partial pressure to the first-order. Taking into account these results together with literature data, the conclusion is reached that although the thermochemical equilibrium decomposition of methane is favored by lower pressure, the rate of methane decomposition is favored by higher pressure.

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II-2. E. F. Aref'eva, et al., Khimiya Tverdogo Topliviva 11, No. 1, 1129-35 (1977)

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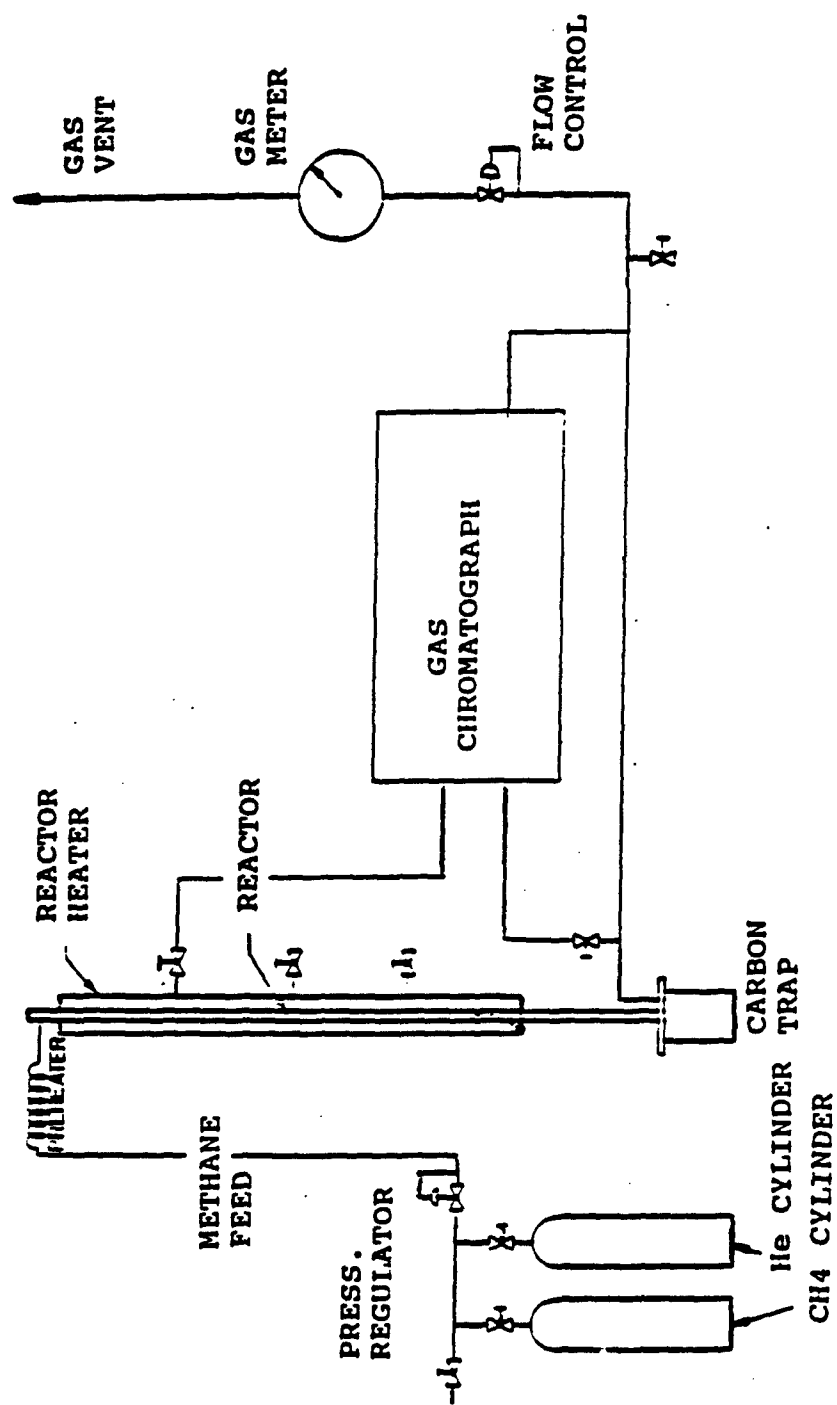
Figure II-1. Schematic Flow Sheet of Tubular Reactor for Methane Decomposition.

# TABLE II-1. EXPERIMENTAL DATA OF METHANE DECOMPOSITION

| Run Number | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Temperature centigrade | 900 | 900 | 900 | 900 | 800 | 800 | 800 | 700 | 700 | 700 | 900 | 900 | 900 | 900 | 900 | 900 |
| Pressure atm | 56.1 | 56.1 | 56.1 | 56.1 | 56.1 | 56.1 | 56.1 | 56.1 | 56.1 | 56.1 | 28.2 | 28.2 | 28.2 | 41.8 | 41.8 | 41.8 |
| Methane concentration in inlet gas vol% | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Exit gas flow rate at standard condition liters / min. (25°C, 1 atm) | 54.34 | 30.24 | 21.89 | 13.85 | 50.57 | 20.6: | 14.89 | 56.61 | 26.96 | 15.06 | 65.58 | 36.53 | 17.25 | 149.0 | 86.99 | 27.24 |
| Residence time sec. based on inlet gas flow rate | 21.8 | 42.3 | 60.5 | 103.0 | 23.7 | 58.9 | 83.6 | 22.8 | 48.3 | 86.8 | 8.94 | 16.8 | 37.0 | 5.54 | 10.3 | 35.7 |
| Methane concentration in exit gas vol% | 78.6 | 65.4 | 59.7 | 48.1 | 92.6 | 89.8 | 85.7 | 97.4 | 95.7 | 95.0 | 81.2 | 72.7 | 66.4 | 90.8 | 75.5 | 61.8 |
| Methane conversion % | 10.7 | 17.3 | 20.2 | 26.0 | 3.7 | 5.1 | 7.2 | 1.3 | 4.3 | 2.5 | 9.4 | 13.7 | 16.8 | 4.6 | 12.3 | 19.1 |

## TABLE II-2.  CALCULATED DATA OF METHANE DECOMPOSITION

| Run Number | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Temperature centigrade | 900 | 900 | 900 | 900 | 800 | 800 | 800 | 700 | 700 | 700 | 900 | 900 | 900 | 900 | 900 | 900 |
| Pressure atm | 56.1 | 56.1 | 56.1 | 56.1 | 56.1 | 56.1 | 56.1 | 56.1 | 56.1 | 56.1 | 28.2 | 28.2 | 28.2 | 41.8 | 41.8 | 41.8 |
| Methane concentration in inlet gas vol% | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Inlet gas flow rate liters/min. at environmental condition | 3.40 | 1.75 | 1.23 | 0.72 | 3.12 | 1.26 | 0.89 | 3.25 | 1.53 | 0.85 | 8.29 | 4.40 | 2.00 | 13.4 | 7.19 | 2.07 |
| Residence time sec. based on inlet gas flow rate *1 | 21.8 | 42.3 | 60.5 | 103.0 | 23.7 | 58.9 | 83.6 | 22.8 | 48.3 | 86.8 | 8.94 | 16.8 | 37.0 | 5.54 | 10.3 | 35.7 |
| Inlet methane conc. mol/liter $C_{CH4O}$ | 0.583 | 0.583 | 0.583 | 0.583 | 0.637 | 0.637 | 0.637 | 0.703 | 0.703 | 0.703 | 0.293 | 0.293 | 0.293 | 0.434 | 0.434 | 0.434 |
| Exit methane conc. mol/liter $C_{CH4}$ | 0.458 | 0.381 | 0.348 | 0.280 | 0.590 | 0.572 | 0.546 | 0.684 | 0.672 | 0.668 | 0.238 | 0.213 | 0.195 | 0.394 | 0.328 | 0.268 |
| Equilibrium conc. mol/liter $C_{CH4E}$ | 0.231 | 0.231 | 0.231 | 0.231 | 0.346 | 0.346 | 0.346 | 0.487 | 0.487 | 0.487 | 0.083 | 0.083 | 0.083 | 0.150 | 0.150 | 0.150 |
| $k_1 \times t$ (-) *2 | 0.246 | 0.457 | 0.578 | 0.976 | 0.073 | 0.109 | 0.158 | 0.026 | 0.044 | 0.052 | 0.210 | 0.325 | 0.423 | 0.097 | 0.288 | 0.516 |

*1:  Reactor Volume  1.236 liters

*2:
$$k_1 \times t = \frac{C_{CH4O} - C_{CH4E}}{C_{CH4O} + C_{CH4E}} \ \ln \frac{C_{CH4O}^2 - C_{CH4} \times C_{CH4E}}{C_{CH4O}\,(C_{CH4} - C_{CH4E})}$$
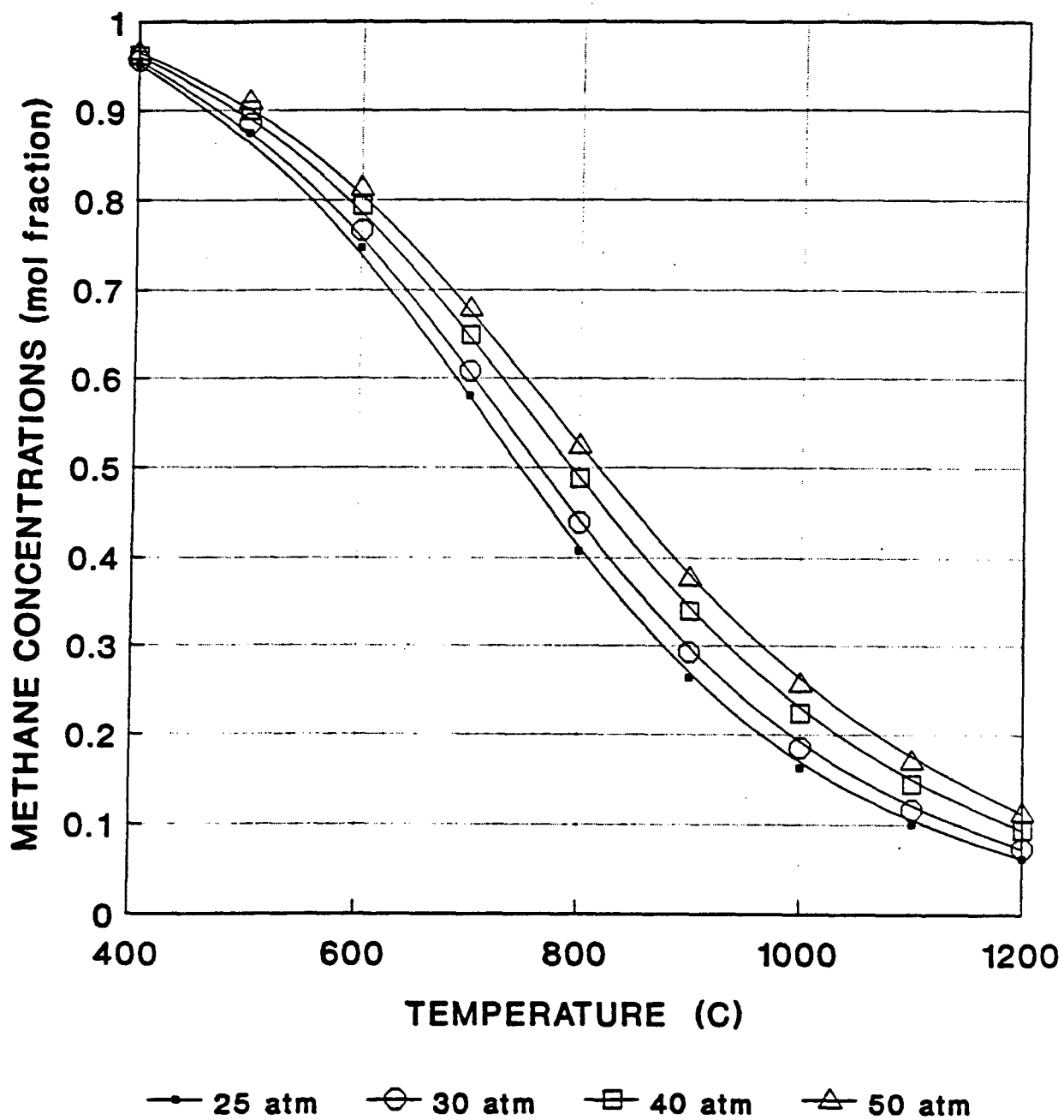
Figure II-2. Equilibrium Data of Methane.
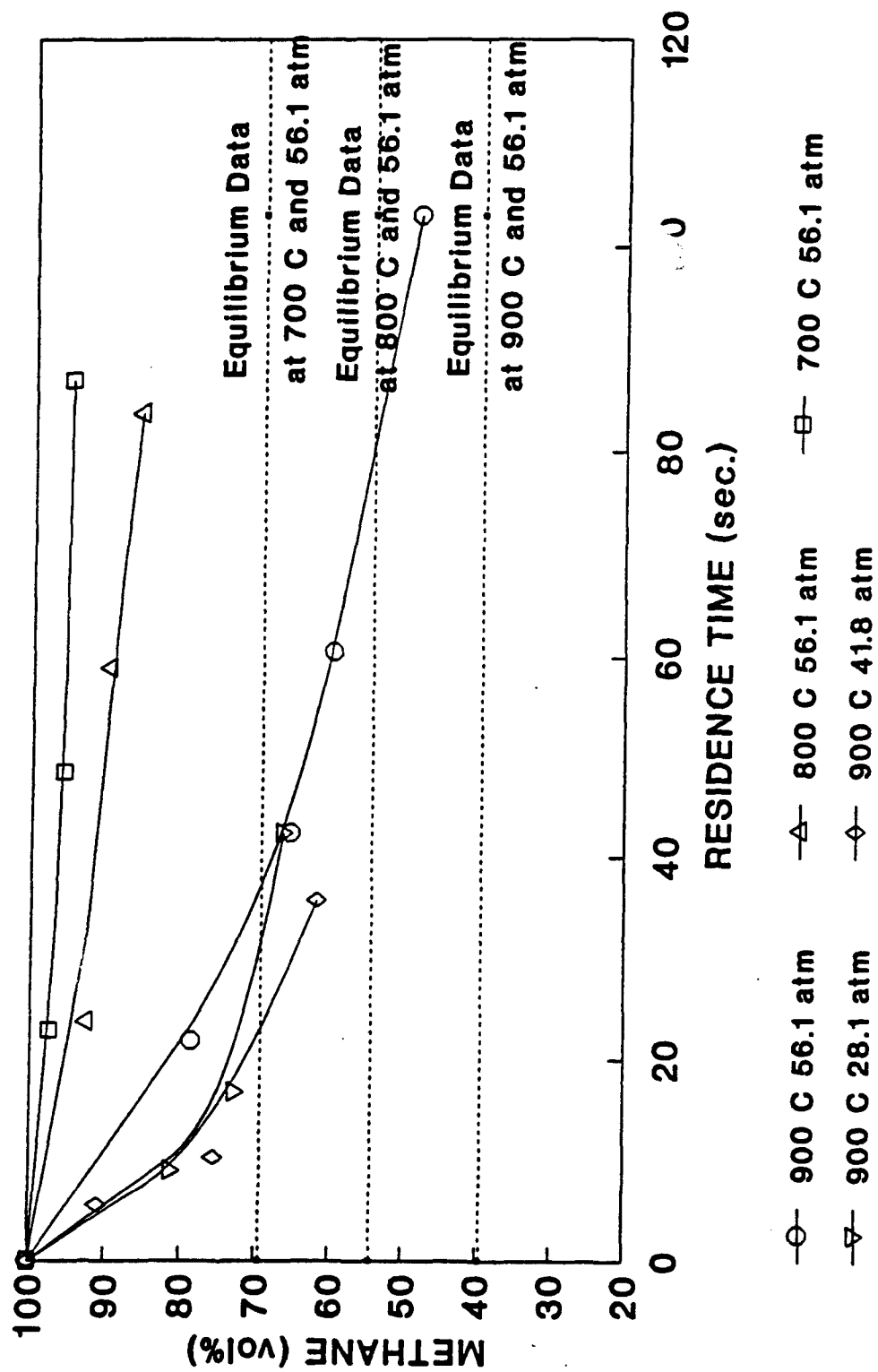
Figure II-3. Methane Concentration vs. Residence Time.

gas inlet ━━━ Fao Qo

Fa

dV

Fa+dFa

tubular reactor

gas outlet
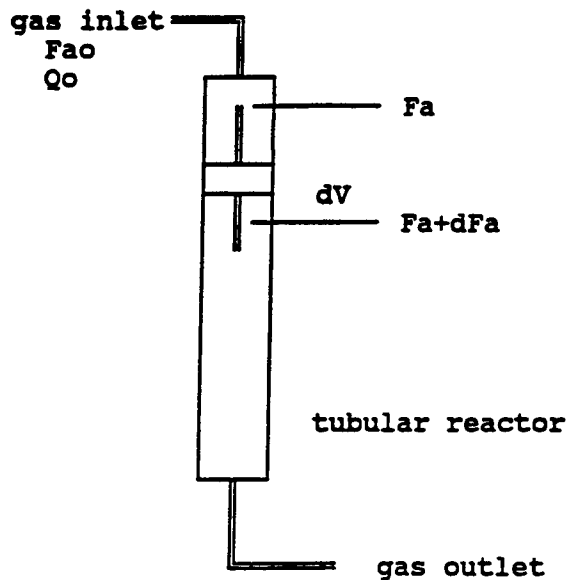
**Tubular Reactor Model**

**Mass Balance of A component**

$$Fa = Fa + dFa + (-r_A) \times dV$$

$$-dFa = (-r_A) \times dV$$

$$Fa = Fao \times (1 - X_A)$$

$$dV/Fao = dX_A/(-r_A)$$

$$Fao = Qo \times Cao$$

$$dV/Qo = Cao \times dX_A/(-r_A)$$

$$dV/Qo = dt$$

$$Ca = Cao \times (1 - X_A)$$

$$-dCa/dt = -r_A$$

Fa :molar velocity (mol/sec)
Q  :volume velocity (liters/sec)
Ca :concentrarion of A component (mol/liter)
$X_A$ :degree of conversion of A component (-)
    Subscript o :initial condition

**Reaction Rate Model**

$$CH_4 \underset{k2}{\overset{k1}{\rightleftharpoons}} C + 2 H_2$$

$$-r_{CH4} = -dC_{CH4}/dt = k1 \times C_{CH4} - k2 \times C_{H2}^2$$

initial condition
  at t = 0      $C_{H2} = 0$
  at equilibrium      $-dC_{CH4}/dt = 0$

solution of differential equation

$$k1 \times t = \frac{C_{CH4O} - C_{CH4E}}{C_{CH4O} + C_{CH4E}} \ln \frac{C_{CH4O}^2 - C_{CH4} \times C_{CH4E}}{C_{CH4O} \times (C_{CH4} - C_{CH4E})}$$

  k1: methane consumption rate constant(1/sec)
  k2: methane production rate constant(liter/sec/mol)
  t : residence time (sec)
  $C_{CH4O}$ :methane initial concentration (mol/liter)
  $C_{CH4}$  :methane concentration of outlet (mol/liter)
  $C_{CH4E}$ :methane equilibrium concentration (mol/liter)

Figure II-4. Tubular Reactor Model and Derivation of Rate Equation.
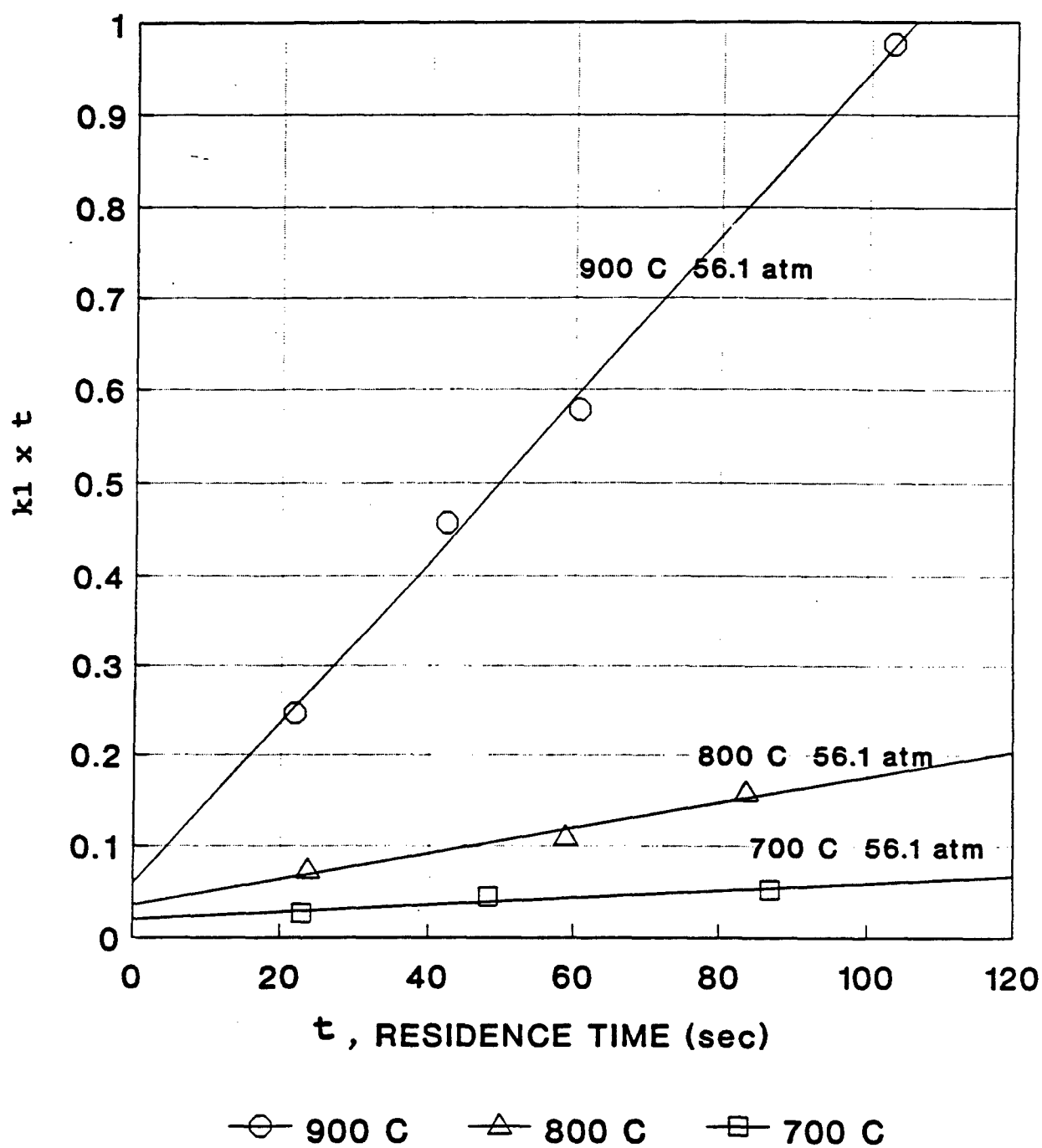
Figure II-5. k1 × T vs. Residence Time at 700 to 900°C and 56.1 atm.

# Arrhenius Plot
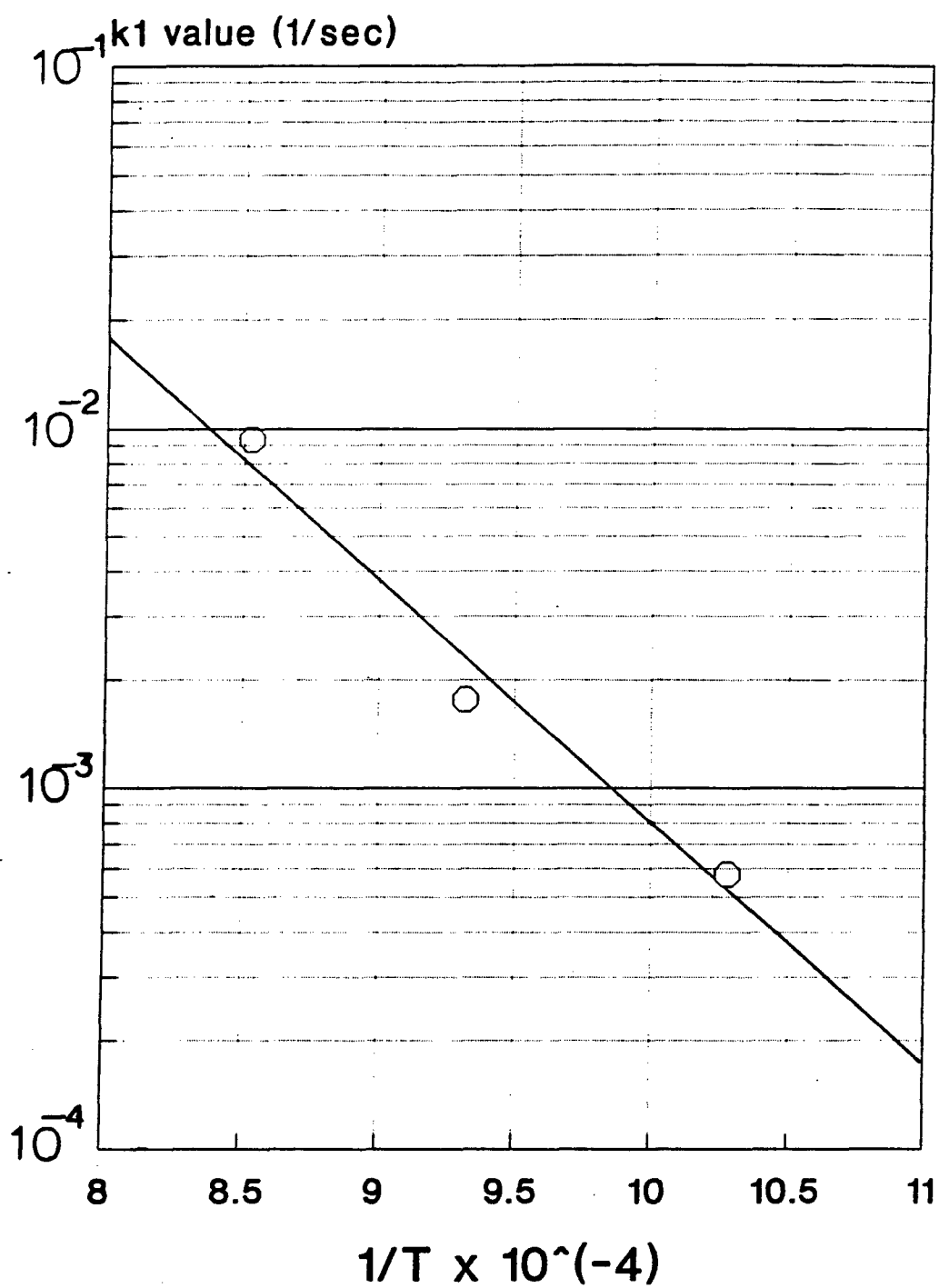


Figure II-6. Rate Constant of Methane Decomposition vs. Recipical Temperature.
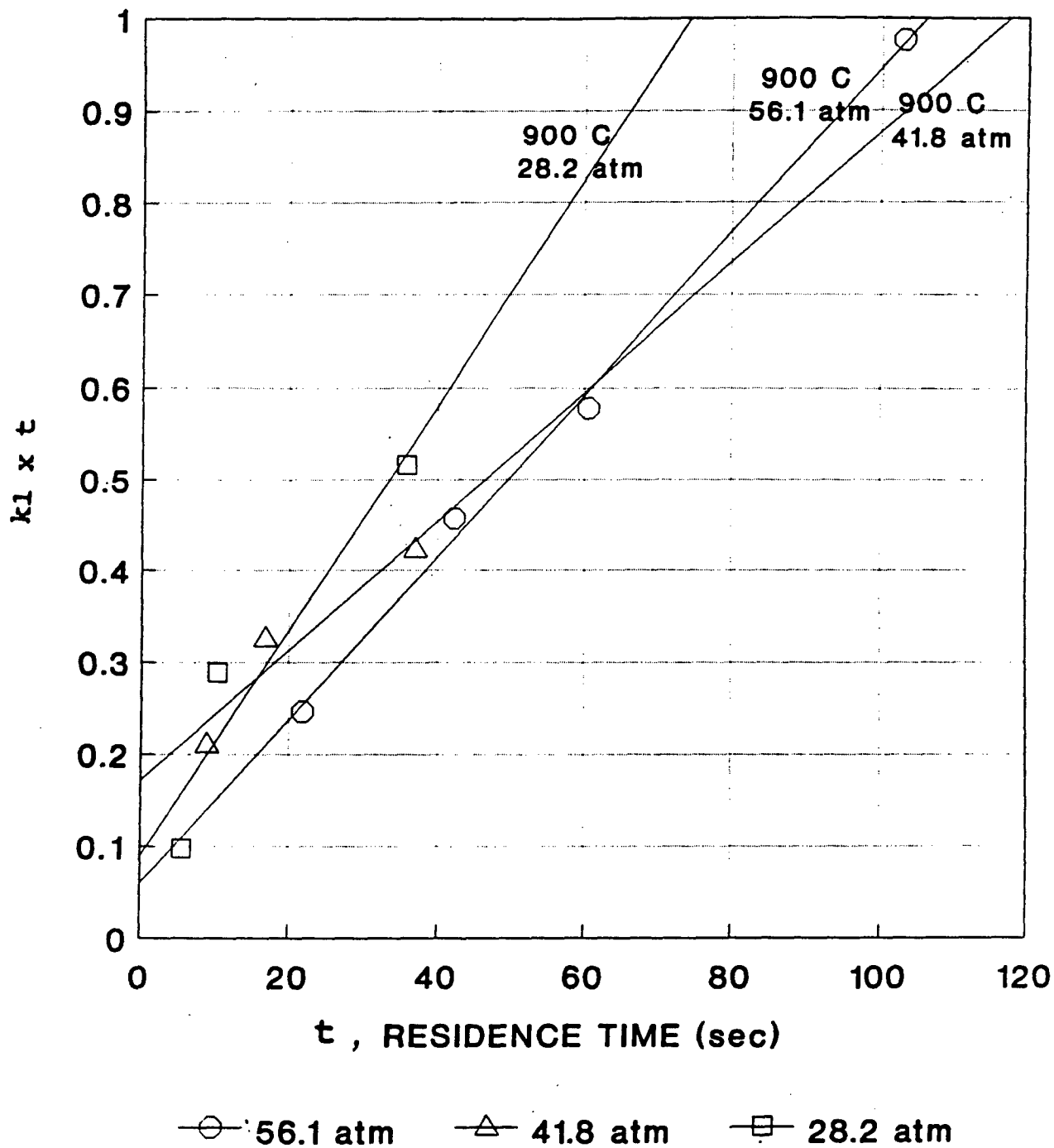
Figure II-7. k1 × t vs. Residence Time at 900°C and 28.2 to 56.1 atm.

Part III

# DESIGN ANALYSIS OF THE HYDROCARB PROCESS
# WITH ALTERNATIVE AND MULTIPLE FEEDSTOCKS

by

YUANJI DONG AND MEYER STEINBERG

HYDROCARB CORPORATION
232 West 40th Street
New York, NY 10018

SUBCONTRACTOR TO

BROOKHAVEN NATIONAL LABORATORY
Upton, NY 11973

# Design Analysis of the Hydrocarb Process
## With Alternative and Multiple Feedstocks

by

Yuanji Dong and Meyer Steinberg

Hydrocarb Corporation
232 West 40th Street
New York, NY 10018

## ABSTRACT

The designed performance of the Hydrocarb process with alternative and multiple feedstocks was investigated. The alternative feedstocks studied for the Hydrocarb process included biomass (wood), Alaska Beluga (sub-bituminous) coal, Kentucky (Bituminous) coal, North Dakota (lignite) coal and Wyodak (sub-bituminous) coal. A Process Simulation Computer Model was used to design the process, and obtain complete energy and mass balances. Boundary conditions of pressure, temperature and mass balances for the cyclical process were determined. The study also included using sludge and digester gas from sewage plants as additional feedstocks. It was found that these feedstocks have to be coprocessed with either biomass or coal to obtain a workable mass balance. The maximum allowable feed ratios of sludge to biomass or sludge to coal were determined. The effect of pressure and temperature for the biomass and sludge feedstock cases were also developed.

# INTRODUCTION

In our previous report,[III-1] an analysis was performed for the Hydrocarb Process to produce methanol and carbon black from biomass (wood) with methane (natural gas) as co-feedstock. The effects of different types of reactors, different process configurations (flowsheet arrangements), as well as operating conditions on process efficiency and product distribution were studied by using the Hydrocarb Process Simulation Program (HCSP) based on the thermodynamic equilibrium in the ternary system C-H-O. The following conclusions were reached in the previous study:

(1) In order to process wood feedstock, methane should be added into the system as required by the stoichiometry. The minimum required methane depends upon the cycle (process configuration) and reactor type used.

(2) A fluidized bed reactor can simplify the procedure for mixing and separation of different kinds of solids, and, therefore, is recommended for use in the Hydrocarb Process.

(3) Cycle 1 is defined as the process configuration in which the hydropyrolyzer (HPR) output is led to the methane pyrolyzer (MPR), and then to the methanol Synthesis reactor (MSR). Cycle 1 usually provides a higher methanol yield than Cycle 2 in which the configurationn is HPR to MSR to MPR. Also Cycle 2 requires two heat exchangers whereas Cycle 1 needs only one.

(4) The reaction temperature in the HPR may be controlled by adjusting the temperature of the process gas into the reactor.

Although the previous report has gained some insight into the main features of the Hydrocarb Process, particularly for the case where wood is used as a feedstock, more work was needed to explore the feasibility of using alternative feedstocks and multiple feedstocks.

Furthermore, Steinberg[III-2,III-3] indicated that the use of biomass through photosynthesis in combination with Hydrocarb Process can offer a solution to the global greenhouse problem, utilizing biomass as a co-feedstock with fossil fuel to produce methanol while

sequestering the carbon can significantly reduce and even eliminate $CO_2$ greenhouse gas emissions to the atmosphere.

A pilot plant project, treating 22.7 kg/hr of sludge and municipal solid waste (MSW) together with methane to produce methanol and carbon black, has been proposed and is being conducted in California. Our preliminary calculation showed that the sludge can not be utilized alone to make up heat balance in the HPR due to its very low heating value. Thus, multiple feedstocks have to be considered. This requires an investigation of multi-feedstock utilizati in the Hydrocarb Process.

A water quality control plant for a large municipality, where a Hydrocarb pilot plant may be built, treats about 113,562 $m^3$ per day of wastewater. It provides 28 tons/day of dried sludge (90% solids content) and, at the same time, produces 13.3 tons/day of digester gas. The latter contains 61.2 mol% $CH_4$ and 37.5 mol% $CO_2$. The question consequently raised here is whether this digester gas can be fed into the process instead of pure pipeline methane.

To meet the above challenge, our program has been extended to treat the case where we can co-feed as many different feedstocks as we wish including digester gas.

In the present study, the following topics are investigated:

(1) Feasibility of using alternative feedstocks:

Kentucky Coal, Alaska Beluga Coal, North Dakota Coal, and Wyodak Coal have been chosen for this study, because they range over a wide variety of ranks and from different locations;

(2) Co-feeding Biomass with Kentucky Coal;

(3) Utilization of sludge and digester gas;

(4) Effects of heat sources for operating the MPR on the process efficiency; and

(5) Pressure and temperature effects on process efficiency.

## BASIC DATA AND DEFINITIONS

Table III-1 lists the basic data of different feedstocks used in this analysis. It should be noted that the heating value here is provided in both English and Metric Units on a dry basis, while the heat of formation is expressed on a moisture and ash free basis.

For each set of feedstocks, both Cycle 1 and Cycle 2 were calculated and compared to each other. Brief flowsheets of Cycle 1 and Cycle 2 are illustrated in Figure III-1. Our previous report[III-1] gives a detailed description of these cycles. In Cycle 1, the process gas at 1000 C from the MPR is cooled down by a gas heat exchanger to around the reaction temperature of the methanol convertor, and this recovered energy is used in the heat exchanger to heat the process gas from the condensers at 50 C up to about the HPR's temperature. When an energy balance is performed, the temperature of process gas into the HPR, $T_7$, is so determined that the reaction heat generated in the HPR is just balanced by the enthalpy difference of inlet and outlet streams. The temperature of process gas into the MSR, $T_5$, is then calculated by the heat balance around the gas heat exchanger. In Cycle 2, two gas exchangers are used as shown in Figure III-1. One exchanger is to cool the gas stream from the temperature of the HPR to the temperature of the MSR by heating up the gas stream coming from the condensers. Before entering the MPR, the process gas is further heated in the second gas heat exchanger by the hot gas stream from the MPR. In this case, the calculation is made to first determine $T_7$ by balancing the heat load of the HPR to be zero. Then, $T_6$ and $T_8$, the temperatures of gas leaving the two heat exchangers can be calculated respectively from the heat balances of the two heat exchangers.

All calculations were made based on the use of fluidized beds for the HPR and the MPR.

The heat source for the MPR could be any of the following fuels: (1) the residual char discharged from the HPR, (2) purge gas discharged from the recycle stream after the condensers, and (3) additional natural gas or solid fuel including any type of coal and biomass. In this study, two cases were investigated: one for burning char, off gas and biomass or digester gas

or fossil fuel; and another for burning off gas and natural gas only without using solid fuel in the combustor.

The carbon conversion of any solid feedstock in the HPR was assumed to be 90%. This may lead to a conservative estimate for wood conversion because of its higher reactivity in the hydrogasifier.

Except for those runs made for investigating the effects of operating conditions, the system pressure was chosen to be 50 atm and the temperatures for the HPR and MPR were 900 and 1000 C respectively. The choice of temperature of 900 C for operation of the HPR is to ensure the effectiveness of sulfur removal with the use of limestone and dolomite. The MPR temperature was chosen by consideration of the state of the art for limitation of the materials of construction. The temperature of the methanol convertor is assumed to be 260 C and the condenser is operated at 50 C. Preliminary calculation showed that these conditions resulted in a satisfactorily high process efficiency (70-80%).

All calculations were made on a capacity basis of 100 tons per calendar day of the major solid feedstock. The actual feed rate into the HPR is equal to the above capacity divided by the operating factor which is assumed to be 90%. Therefore, for a 100 tons per calendar day plant of an as-received coal, for instance, the feed rate of this feedstock into the HPR is 100/0.9 = 111.1 tons/day or 4629.6 kg/h if no drying is needed before feeding into the HPR.

When a single solid feedstock was tested, the strategy of calculation is shown in Figure III-2. First of all, an as-received (AR) undried feedstock is tried to see whether a material and energy balance can be achieved. If the answer is positive, then feeding additional water into the HPR may be tried until a maximum allowable value of additional water is found. If the balance can not be made for the AR feedstock, two approaches may be tried depending on whether the material balance or the energy balance is in question. If the material balance fails, co-feeding some methane into the HPR may be the way to make up the balance. A minimum $CH_4$ requirement is then calculated. However, $CH_4$ has little effect on the heat load of the

HPR. Thus, if the HPR is endothermic in spite of adjusting the temperature of the inlet gas, drying the feedstock may be necessary and the calculation then is aimed at obtaining the maximum allowable moisture of feedstock. In some cases, both adding methane and drying feedstock may be needed to obtain a workable cycle.

When multiple feedstocks are investigated, and sludge is used as one of the feedstocks, the digester gas is always assumed as a co-feedstock. Considering its availability in the Riverside Water Quality Sewage Plant in California, the weight ratio of digester gas to sludge was set as 0.5. The calculations were aimed at obtaining a maximum allowable sludge feed rate.

In the calculation, limestone feed rate is determined by assuming a molar ratio of Ca to S of 2. The composition of $CaCO_3$ in limestone is assumed to be 70%, and the rest being ash.

# RESULTS AND DISCUSSION

## SINGLE SOLID FEEDSTOCK

### Alaska Beluga (Sub-Bituminous) Coal:

Table III-2 shows that, for Cycle 1, as-received (AR) Beluga coal has to be dried from 21.78% of moisture to 11% before it can be fed into the HPR in order to obtain material and energy balances. If the coal is directly used without drying, there would be a minimum requirement for methane co-feedstock at a ratio of 5 wt.% to the as-received Beluga coal. Since the water may react with carbon to form CO, the use of the as-received Beluga coal greatly increases the methanol production and improves the methanol ratio in the product streams. The latter case also showed about a 2% higher thermal efficiency compared to the drying case. ʳ· is also found in most of the calculations that, if the residual char discharged from the HPR is used together with other heat sources for the MPR, it reduces the consumption of other fuels for combustion and provides an increase of about 5% in thermal efficiency. A comparison of the results of Cycle 1 with Cycle 2 for Beluga coal shows that Cycle 2 can directly use as-received Beluga coal without the need to dry the coal. Furthermore, additional water is allowable for feeding into the HPR with as-received coal. The gas circulation for Cycle 2 is relatively less than that for Cycle 1. However, Cycle 2 usually produces more carbon and less methanol in comparison with Cycle 1, and its thermal efficiency is lower.

### Kentucky (Bituminous) Coal:

It was found from Table III-2 that, when as-received Kentucky coal is used alone as a single solid feedstock, the material and energy balances can be established for both Cycle 1 and Cycle 2. For Cycle 1, an additional amount of water can be co-fed into the HPR at a maxi-

mum allowable content of 29 wt.% of the as-received Kentucky coal according to the material and energy balance. For Cycle 2, the allowable additional water is as high as 67 wt.% of the coal. The addition of the water for Cycle 1 improves the thermal efficiency (the ratio of the total heating value of carbon and methanol to the total heating value of feedstocks and methane), however, its effect in Cycle 2 is the reverse. The gas circulation rate appears higher than when Beluga coal is used. The thermal efficiency for Cycle 2 is better than for Cycle 1 if as-received Kentucky coal is used alone.

North Dakota (Lignite) Coal:

Table III-2 shows that neither Cycle 1 and Cycle 2 can use North Dakota lignite alone without drying. For Cycle 1, in addition to drying the coal from 30.1 wt% moisture to 5 wt%, a minimum methane feed rate of 2 wt.% of the coal has to be co-fed into the HPR; for Cycle 2, the coal is required to be dried down to only 15 %. Cycle 2 gives a 5 % lower thermal efficiency than Cycle 1.

Wyodak (Sub-Bituminous) Coal:

The results in Table III-2 indicate that Wyodak coal also needs drying when it is fed alone into the HPR for Cycle 1. The maximum allowable moisture in this case is 13 wt.%. For Cycle 2, however, as-received Wyodak coal can be used. The results also show that the maximum additional water rate is 7 wt.% of the coal for Cycle 2. Residual char burning may raise the thermal efficiency by an additional 4-5%, which is essentially similar to the results obtained for other feedstocks.

Biomass (Wood):

The calculated results for wood feedstock, as listed in Table III-2, show the necessity of co-feeding methane for both Cycles when as-received wood is directly fed into the HPR.

The required minimum methane feed rate is 15 wt.% of the as-received wood for Cycle 1; while Cycle 2 needs a methane rate of only 6 wt.%. It can be seen that, in general, the product ratio (methanol/pure carbon) for wood as feedstock is relatively higher, and more methanol and less carbon black are produced in comparison with other feedstocks. It also shows that Cycle 1 has a higher thermal efficiency than Cycle 2.

The computer printout for Cycle 1 under 100 tons per calendar day of wood and 15 tons per calendar day of methane feed rate conditions is shown in Appendix III-1. Figure III-3 summarizes the flow rates, compositions and temperatures of the major streams in the system. After purging a small amount of off-gas (3 kgmol/hr) for use with other fuels (char, biomass and methane) to heat up the MPR, the temperature of the remaining process gas of 2170 kgmol/hr from the condenser is raised up to 927 C by the gas heat exchanger to meet the requirement of a neutral energy balance around the HPR. In the gas heat exchanger, the heat is provided by recovering the energy from the process gas at 1000 C leaving the MPR. The calculated temperature of the hot gas stream leaving the heat exchanger is 257 C which then enters the methanol converter. The residual char of 212 kg/hr is discharged from the HPR and is then burned in the combustor together with the 3 kmol/hr of off-gas and 1546 kg/hr of wood to provide the heat required by the endothermic reactions in the MPR. Thus, the total wood consumption for producing 3192 kg/hr of methanol and 1222 kg/hr of carbon black is 6176 kg/hr, of which about one fourth is used for combustion. The use of wood as fuel is desirable because it is produced by photosynthesis and its net $CO_2$ emission is zero.

## MULTIPLE-FEEDSTOCKS WITH SEWAGE SLUDGE AND DIGESTER GAS

Since sludge has quite a low heating value, in order to maintain a desired temperature in the HPR, the utilization of sludge has to be accompanied by biomass and/or other fossil fuel. In this study, wood, Kentucky coal and Wyodak coal are used as co-feedstock with sludge respectively to calculate the possible maximum capacity of sludge. The feed rate of digester

gas is always kept at 50 wt.% of the sludge rate, according to the gas availability in a water quality control plant. The calculated results are summarized in Table III-3.

### Sludge with Wood:

When sludge is treated together with wood, methane must be used as a co-feedstock at a rate of 15 wt% of wood. It was found that, for Cycle 1, both wood and sludge have to be dried before being used. The sludge was assumed to be dried to contain 5 wt% moisture, and its feed ratio is dependent upon the moisture content of the dried wood. Figure III-4 plots the product ratio of methanol to carbon and the thermal efficiency as functions of sludge feed rate. It shows that both methanol production and thermal efficiency increase with the ratio of sludge feed rate to the wood feed rate. There is a maximum allowable sludge feed ratio in order to maintain a desired reaction temperature in the HPR. When wood is dried to 5 wt% moisture and fed with 15 wt% of methane, the allowable maximum feed ratio of sludge to wood is 70 wt%. If wood is further dried to 1 wt% moisture, the feed ratio of sludge increases to 80 wt%. For Cycle 2, as-received wood and as-received sludge can be used with a maximum sludge feed rate of 50 wt%. If a dried wood of 5 wt% moisture is used, the sludge feed ratio reaches 90 wt%. However, comparing the two cycles, Cycle 2 has a lower thermal efficiency, and it produces more carbon and less methanol, though its gas circulation requirement is slightly smaller. It is interesting to note in Appendix III-2, that with feeding digester gas into the HPR, the $CO_2$ component reacts in the HPR to form CO and $CH_4$, thus increasing the CO mole fraction in the process gas from 2.4% to 6.2%. These constituents are then converted to methanol and carbon black in the following steps. This ability for the HYDROCARB Process to convert $CO_2$ in the clean fuels should be significant for greenhouse gas mitigation. Figure III-5 summarizes the calculation results for this case.

### Sludge with Kentucky Coal:

When Kentucky coal is used as co-feedstock with sludge, it was found that a methane cofeedstock is unnecessary. The coal and sludge can be used without drying. In Table III-3, the allowable maximum feed ratio of sludge to the as-received coal is 4:1 for Cycle 1 and 1.7 for Cycle 2. It shows that Cycle 1 has a much higher treatment ability for sludge.

### Sludge with Wyodak Coal:

Wyodak coal can also be used as a co-feedstock with sludge. The results in Table III-3 show that as-received Wyodak coal can not make up the heat balance in the HPR and it has to be dried down to 5 wt% moisture. However, as-received sludge can be used in both cycles. For Cycle 1, the maximum allowable co-feeding rate of sludge is 120 wt%. In Cycle 2, only 90 wt% sludge can be fed together with Wyodak coal of 5 wt% moisture content.

## PRESSURE AND TEMPERATURE EFFECTS

The effects of pressure and temperature on process efficiency and product distribution were investigated for the Alaska Beluga coal. Table III-4 summarizes the calculated results. The following trends can be found from the Table:

(i) The minimum required methane feed per unit of biomass increases with a decrease in system pressure.

(ii) The maximum allowable moisture in the coal decreases with a decrease in system pressure.

(iii) The product distribution of methanol vs. carbon decreases with a decrease in system pressure.

(iv) Higher temperatures in the HPR and MPR promote higher methanol production and higher thermal efficiency.

These trends, of course, are limited by the thermal and structural properties of the materials of construction used. Taking these factors into account leads to recommending the operating conditions of 50 atm and 900 C for the HPR and 1000 C for the MPR.

# CONCLUSIONS

(1) Cycle 1 usually provides a higher process efficiency and more methanol production than Cycle 2. Thus, Cycle 1 is recommended for most cases.

(2) Burning residual char for heating up the MPR increases the thermal efficiency of the process by about 4 to 5% compared to that of the process without burning residual char.

(3) Beluga coal can be fed with natural gas without drying. However it has to be dried when used alone, and the maximum allowable moisture content is 11 wt%.

(4) Kentucky coal (8.6 % moisture) can be processed without drying, in which case additional water may be co-fed to improve thermal efficiency and methanol and carbon product distribution.

(5) North Dakota coal and Wyodak coal, which have over 26% moisture, have to be dried before being used as a single solid feedstock.

(6) As-received (AR) biomass (wood) together with 15 wt% of methane produces a 2.6:1 weight ratio of product methanol to carbon black. The thermal efficiency is about 75%.

(7) Sludge can be processed together with woody biomass or coal. The maximum feed ratio of sludge to wood is 0.7 if both sludge and wood are dried to 5 wt% moisture, and the feed ratios of methane and digester gas are 0.15 and 0.35, respectively. The thermal effeciency in this case is 76%. The methanol product ratio to carbon black is 2.19.

(8) $CO_2$ in the digester gas can be converted to CO in the hydrogasifier (HPR), which is further converted to carbon and methanol in the methane pyrolyzer (MPR) and the methanol converter. The ability of converting $CO_2$, which causes global greenhouse problems, to the useful clean fuels, methanol and carbon black, is an attractive feature of the Hydrocarb Process, especially if biomass is used as co-feedstock.

(9) This study showed that there is a need to systematically investigate the important effects of feedstock composition based on both material and energy balances to determine the allowable operational zone in the thermodynamic equilibrium ternary system, C-H-O.

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III-3. Borgwardt, R.H., Steinberg, M., Grohse, E.W. and Tung, Y.: *"Biomass and Fossil Fuel to Methanol and Carbon via the Hydrocarb Process,"* presented at the <u>Conference on Energy from Biomass and Wastes XV</u>, Washington DC, March 27, 1991

# TABLE III-I.  BASIC DATA FOR THE FEEDSTOCKS USED IN THE STUDY

| Feedstock | Biomass Wood | Kentucky Coal | N.Dakota Coal | Wyodak Coal | Beluga Coal | Sewage Sludge |
|---|---|---|---|---|---|---|
| **Composition (wt%)** | | | | | | |
| C | 45.86 | 67.02 | 43.37 | 49.95 | 49.33 | 28.55 |
| H | 5.27 | 4.54 | 2.78 | 3.51 | 4.00 | 4.09 |
| O | 36.07 | 7.22 | 13.97 | 12.58 | 15.56 | 16.03 |
| $H_2O$ | 11.67 | 8.60 | 30.10 | 26.40 | 21.78 | 9.82 |
| Ash | 0.66 | 8.34 | 8.30 | 6.03 | 8.67 | 36.53 |
| S | 0.04 | 2.85 | 0.81 | 0.60 | 0.12 | 1.36 |
| N | 0.43 | 1.43 | 0.67 | 0.93 | 0.54 | 3.62 |
| **Heating Value (Higher)** | | | | | | |
| (BTU/lb-MF) | -8800.0 | -13650 | -10254 | -11730 | -11082 | -5510 |
| (kcal/kg-MF) | -4888.9 | -7583.3 | -5696.7 | -6516.7 | -6156.7 | -3061.1 |
| **Heat of Formation** (kcal/kg-MAF) | -1214.4 | 183.0 | -593.0 | -461.7 | -584.9 | -1769.7 |
| **Heat Capacity** (kcal/kgMF/C) | 0.570 | 0.315 | 0.315 | 0.315 | 0.315 | 0.250 |

MAF  --  Moisture Ash Free
MF  --  Moisture Free

Coal Rank:   Kentucky coal - bituminous
             N. Dakota coal - lignite
             Wyodak coal - sub-bituminous
             Beluga coal - sub-bituminous

## TABLE III-2 RESULTS WITH SINGLE SOLID FEEDSTOCK.
### (p=50atm/HPR=900 C/MPR=1000 C)

| CYC | Feedstocks t/d | Comb. | Carb t/d | MeOH t/d | PR | Ceff % | Teff % | GCR kmol/h |
|---|---|---|---|---|---|---|---|---|
| 1 | 11B100* | TG11 | 32.3 | 32.4 | 1.0 | 77.1 | 68.2 | 1897 |
| 1 | 11B100 | CTG8 | 32.3 | 32.4 | 1.0 | 80.2 | 72.7 | 1897 |
| 1 | AB100+G5 | TG12 | 29.3 | 49.6 | 1.7 | 77.3 | 70.7 | 2007 |
| 1 | AB100+G5 | CTG9 | 29.3 | 49.6 | 1.7 | 80.2 | 74.8 | 2007 |
| 2 | AB100 | TG11 | 34.5 | 23.5 | .68 | 74.9 | 62.9 | 1769 |
| 2 | AB100 | CTG8 | 34.5 | 23.5 | .68 | 77.8 | 67.0 | 1769 |
| 2 | AB100+H11 | TG15 | 32.3 | 32.4 | 1.0 | 73.0 | 62.4 | 1941 |
| 2 | AB100+H11 | CTG12 | 32.3 | 32.4 | 1.0 | 75.7 | 66.2 | 1941 |
| 1 | AK100 | CTK2 | 50.7 | 16.8 | .33 | 83.1 | 68.8 | 2477 |
| 1 | AK100 | TG5 | 50.7 | 16.8 | .33 | 80.3 | 64.0 | 2477 |
| 1 | AK100+H29 | CTK22 | 38.9 | 56.9 | 1.5 | 74.0 | 72.8 | 2541 |
| 1 | AK100+H29 | TG15 | 38.9 | 56.9 | 1.5 | 76.8 | 68.5 | 2541 |
| 2 | AK100 | CT | 52.1 | 7.7 | .15 | 83.9 | 73.4 | 2145 |
| 2 | AK100 | TG1 | 52.1 | 7.7 | .15 | 80.8 | 63.2 | 2145 |
| 2 | AK100+H67 | CTK37 | 38.8 | 57.3 | 1.5 | 65.7 | 64.7 | 2872 |
| 2 | AK100+H67 | TG23 | 38.8 | 57.3 | 1.5 | 71.4 | 61.3 | 2872 |
| 1 | 5N100+G2 | CTN23 | 32.1 | 22.0 | .68 | 73.9 | 72.1 | 1745 |
| 1 | 5N100+G2 | TG9 | 32.1 | 22.0 | .68 | 77.8 | 67.6 | 1745 |
| 2 | 15N100 | CTN28 | 33.0 | 16.2 | .49 | 70.3 | 67.8 | 1546 |
| 2 | 15N100 | TG11 | 33.0 | 16.2 | .49 | 75.6 | 63.6 | 1546 |
| 1 | 13Y100 | CTY22 | 33.8 | 29.4 | .87 | 73.8 | 72.8 | 1925 |
| 1 | 13Y100 | TG11 | 33.8 | 29.4 | .87 | 77.3 | 68.2 | 1925 |
| 2 | AY100 | CTY26 | 35.0 | 24.4 | .70 | 70.2 | 67.3 | 1813 |
| 2 | AY100 | TG12 | 35.0 | 24.4 | .70 | 74.6 | 63.2 | 1813 |
| 2 | AY100+H7 | CTY33 | 33.6 | 30.0 | .89 | 67.5 | 66.8 | 1919 |
| 2 | AY100+H7 | TG15 | 33.6 | 30.0 | .89 | 73.4 | 62.9 | 1919 |
| 1 | AW100+G15 | CTW33 | 26.4 | 69.0 | 2.6 | 72.2 | 74.9 | 2167 |
| 1 | AW100+G15 | TG14 | 26.4 | 69.0 | 2.6 | 77.7 | 71.6 | 2167 |
| 2 | AW100+G6 | CTW39 | 32.9 | 33.6 | 1.0 | 66.7 | 64.7 | 1997 |
| 2 | AW100+G6 | TG15 | 32.9 | 33.6 | 1.0 | 73.5 | 61.4 | 1997 |

A -- As Received
B -- Beluga Coal
C -- Char
G -- Natural Gas
H -- Water
K -- Kentucky Coal
N -- North Dakota Coal
T -- Purged Off Gas
W -- Wood
Y -- Wyodak Coal

CYC -- Cycle
Comb.-- MPR heat sources by combustion
C -- Carbon black product
MeOH -- Methanol product
PR -- Product Weight Ratio (MeOH/C)
Ceff -- Carbon efficiency
Teff -- Thermal efficiency
GCR -- Gas circulation rate

* 11B100 means that 100 t/d Beluga coal is dried to 11% moisture.

## TABLE III-3 RESULTS OF HYDROCARB PROCESS WITH MULTIPLE FEEDSTOCKS.
(p=50atm / HPR=900 C / MPR=1000 C)

| CYC | Feedstocks tons/day | Comb. t/d | C t/d | MeOH t/d | PR | Ceff % | Teff % | GCR kgmol/h |
|---|---|---|---|---|---|---|---|---|
| 1 | 5W100+5S70+G15+D35* | TG20 | 46.6 | 102 | 2.2 | 78.9 | 72.9 | 3520 |
| 1 | 5W100+5S70+G15+D35 | CTW49 | 46.6 | 102 | 2.2 | 73.7 | 76.0 | 3520 |
| 1 | 1W100+5S80+G15+D40 | TG20 | 50.7 | 102 | 2.0 | 79.3 | 72.8 | 3697 |
| 1 | 1W100+5S80+G15+D40 | CTW47 | 50.7 | 102 | 2.0 | 74.5 | 76.0 | 3697 |
| 2 | AW100+AS50+G15+D25 | TG10 | 51.2 | 47.3 | .92 | 76.6 | 64.2 | 2936 |
| 2 | AW100+AS50+G15+D25 | CTW20 | 51.2 | 47.3 | .92 | 75.3 | 67.3 | 2936 |
| 2 | 5W100+AS90+G15+D45 | TG11 | 65.4 | 55.0 | .84 | 77.4 | 65.0 | 3605 |
| 2 | 5W100+AS90+G15+D45 | CTW21 | 65.4 | 55.0 | .84 | 76.4 | 68.0 | 3605 |
| 1 | AK100+AS400+D200 | TG65 | 140 | 297 | 2.1 | 78.8 | 74.4 | 10488 |
| 1 | AK100+AS400+D200 | CTD149 | 140 | 297 | 2.1 | 80.8 | 77.4 | 10488 |
| 2 | AK100+AS170+D85 | TG15 | 107 | 60.3 | .57 | 78.7 | 65.6 | 5154 |
| 2 | AK100+AS170+D85 | CTG21 | 107 | 60.3 | .57 | 81.2 | 69.2 | 5154 |
| 1 | 5Y100+AS120+D60 | TG26 | 63.7 | 103 | 1.6 | 78.5 | 72.9 | 4304 |
| 1 | 5Y100+AS120+D60 | CTD58 | 63.7 | 103 | 1.6 | 80.8 | 76.4 | 4304 |
| 2 | 5Y100+AS90+D45 | TG13 | 68.2 | 37.3 | .55 | 78.1 | 65.9 | 3271 |
| 2 | 5Y100+AS90+D45 | CTD23 | 68.2 | 37.3 | .55 | 80.7 | 69.6 | 3271 |

| | | | |
|---|---|---|---|
| A - As Received | CYC -- Cycle |
| C - Char | Comb.-- MPR heat sources by combustion |
| D -- Digester Gas | C -- Carbon black product |
| G -- Natural Gas | MeOH -- Methanol product |
| H -- Water | PR -- Product Ratio (MeOH/C) |
| K -- Kentucky Coal | Ceff -- Carbon efficiency |
| S -- Sludge | Teff -- Thermal efficiency |
| T -- Purged Off Gas | GCR -- Gas circulation rate |
| W -- Wood | |
| Y -- Wyodak Coal | |

* 5W100+5S70+G15+D35 means that the feedstocks consist of 100 t/d wood which is dried to 5% moisture, 70 t/d sludge which is also dried to 5% moisture, 15 t/d methane and 35 t/d digester gas.

## TABLE III-4 EFFECTS OF PRESSURE AND TEMPERATURE ON PROCESS EFFICIENCY AND PRODUCT DISTRIBUTION.
### (100 t/day of Beluga coal)

| CYC | P atm | T(HPR/MPR) C | Moist % | CH4/Coal | MeOH/C | Ceff % | Teff % |
|-----|-------|--------------|---------|----------|--------|--------|--------|
| 1 | 50 | 900/1000 | 21.78 | .05 | 1.67 | 77.3 | 70.7 |
| 1 | 50 | 900/1000 | 11 | 0 | 1 | 77.1 | 68.2 |
| 1 | 50 | 800/900 | 21.78 | .05 | 0.59 | 78.7 | 66.0 |
| 2 | 50 | 900/1000 | 21.78 | 0 | 0.67 | 74.9 | 62.8 |
| 2 | 50 | 800/900 | 21.78 | 0 | 0.09 | 77.5 | 61.2 |
| 1 | 35 | 800/900 | 21.78 | .05 | 0.71 | 70.8 | 56.8 |
| 1 | 35 | 800/900 | 5 | .05 | 0.29 | 76.8 | 60.1 |
| 1 | 35 | 800/900 | 5 | .1 | 0.26 | 78.9 | 60.9 |
| 2 | 35 | 800/900 | 5 | .05 | 0.04 | 78.9 | 61.2 |
| 2 | 35 | 800/900 | 21.78 | .05 | 0.06 | 75.4 | 56.8 |
| 2 | 35 | 800/900 | 5 | .1 | 0.04 | 80.2 | 72.3 |
| 1 | 30 | 800/900 | 5 | .15 | 0.24 | 80.3 | 68.4 |
| 2 | 30 | 800/900 | 5 | .1 | 0.03 | 80.2 | 71.4 |
| 2 | 30 | 800/900 | 5 | .15 | 0.03 | 81.3 | 81.9 |
| 2 | 30 | 800/900 | 21.78 | .15 | 0.05 | 78.2 | 71.0 |

## CYCLE 1
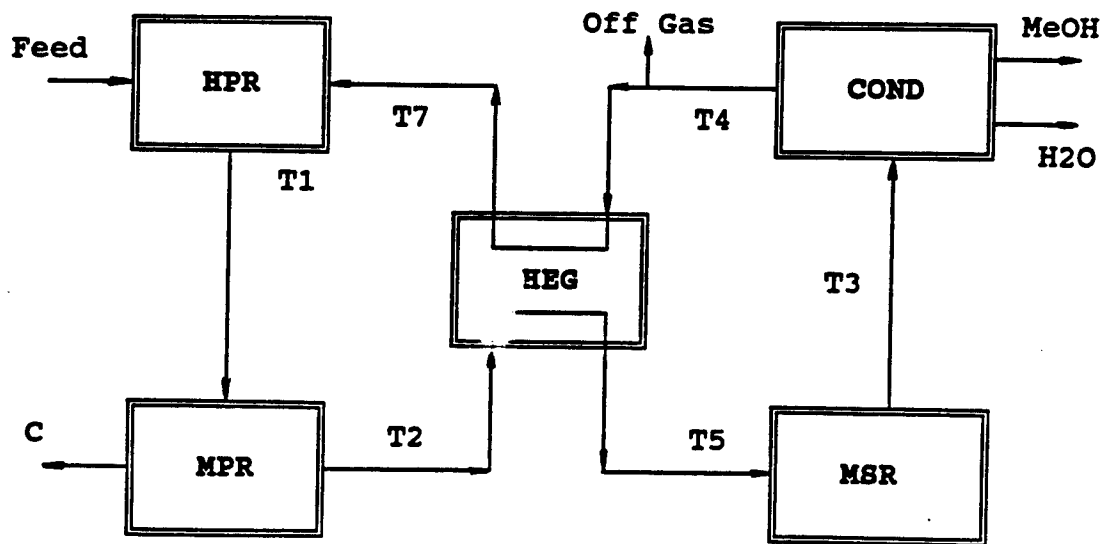


## CYCLE 2
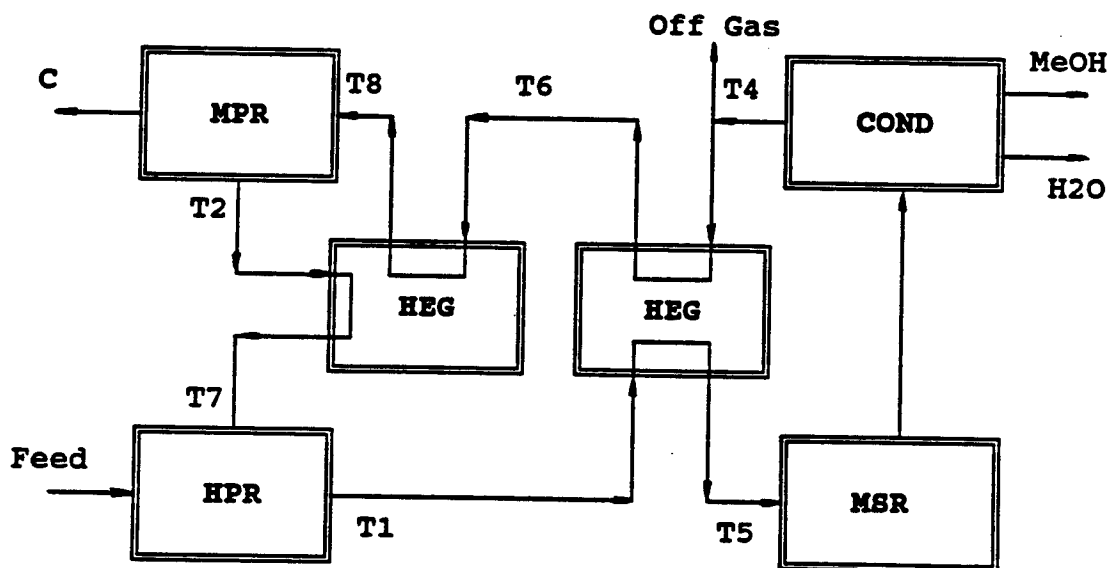


Figure III-1. Brief illustration of Cycle 1 and Cycle 2.
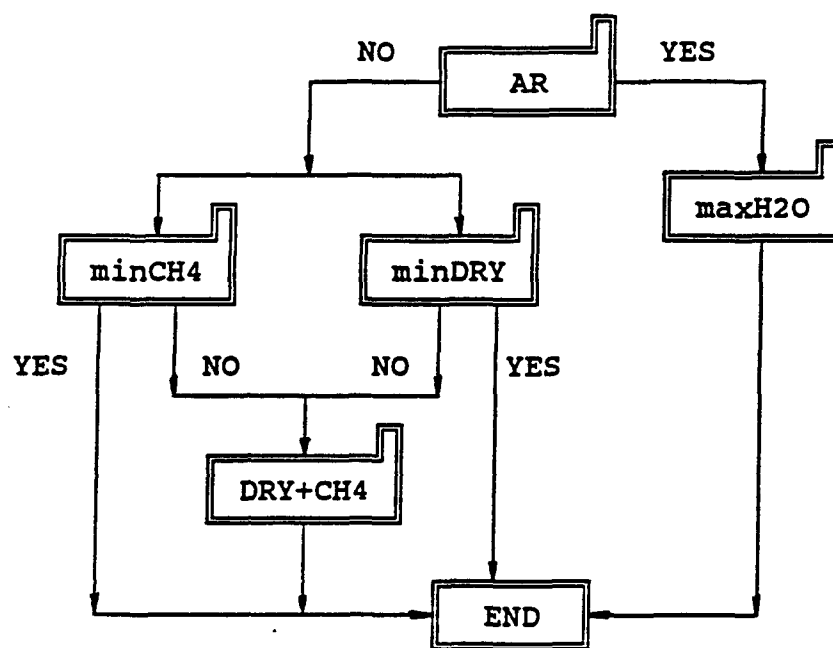
Figure III-2. Strategy of computer calculation for a single solid feestock.

# HYDROCARB PROCESS (CYCLE 1)

## (Biomass   NG)

## (P = 50 atm)

```
                              Off Gas
                              3 kmol/h
                              CO    2.7
Wood 4630 kg/h                CO2   3.0            H2O 620 kg/h
NG      694 kg/h              CH4  24.0
                              H2O   0.1
                              H2   69.5

    ┌──────────────┐                         ┌──────────────┐
    │     HPR      │  927 C                   │     COND     │
    │              │                          │              │
    │    900 C     │                          │    50 C      │
    └──────────────┘                          └──────────────┘
         │  900 C              50 C                 MeOH
         │  2298 kmol/h        2167 kmol/h          3192 kg/h
  Char   │  CO    6.8
  212 kg/h  CO2   0.7                          260 C
         │  CH4  30.1     ┌──────────┐         2304 kmol/h
         │  H2O   6.8     │          │         CO     2.6
         │  H2   55.7     │    HE    │         CO2    2.8
                          │          │         CH4   22.5
                          └──────────┘         H2O    1.6
                                               H2    65.4
                                               MeOH   5.1
    ┌──────────────┐                         ┌──────────────┐
    │     MPR      │ 1000 C      257 C        │    MeOH      │
    │              │                          │              │
    │    1000 C    │                          │   260 C      │
    └──────────────┘                          └──────────────┘
         │           2540 kmol/h
         │           CO    9.2
         │           CO2   0.3
    C 1222 kg/h      CH4  20.4
                     H2O   3.7
                     H2   66.4
```
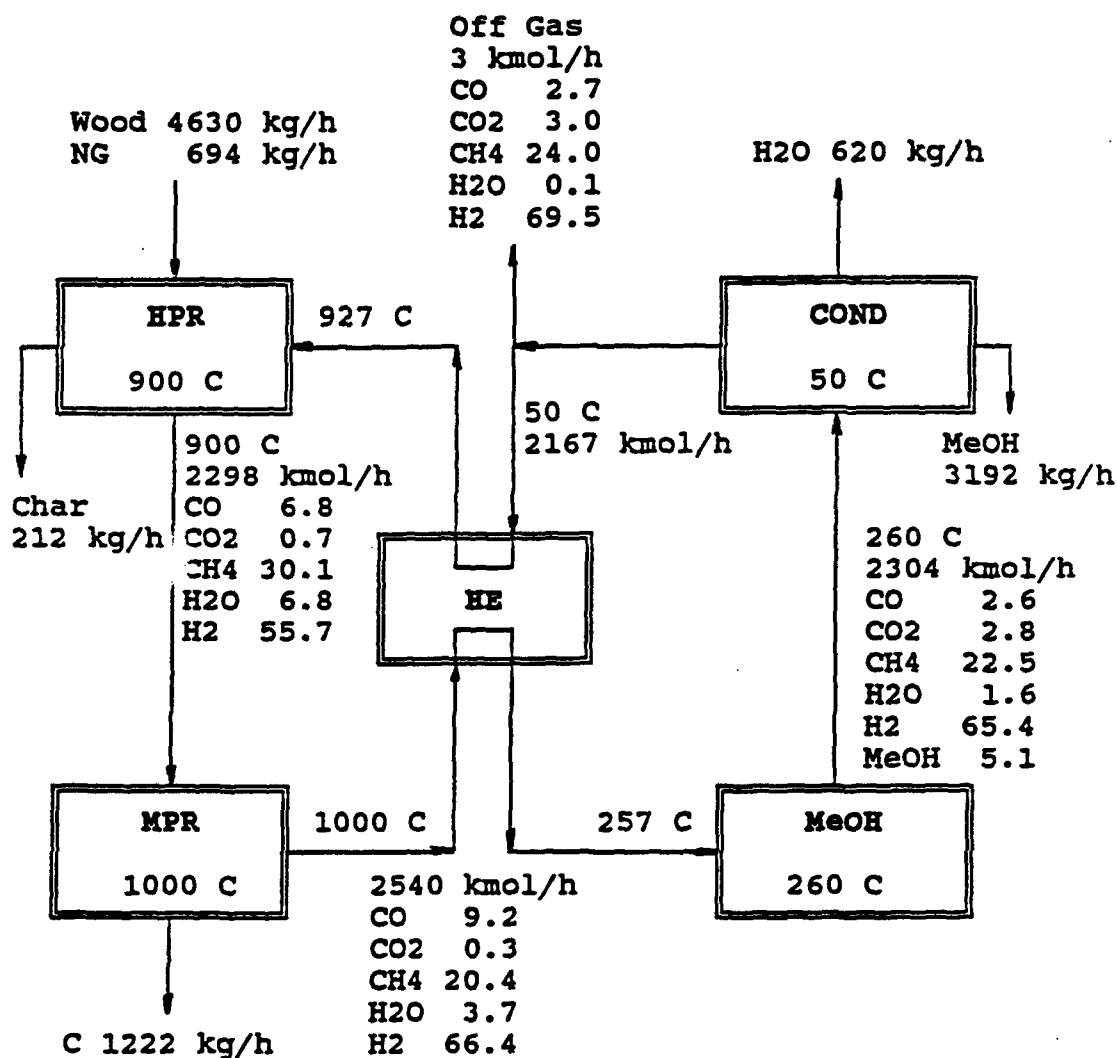
Carbon Conversion of Feedstock in HPR: 90%
Carbon Efficiency: 72.2%
Thermal Efficiency: 74.9%

Figure III-3.  Data su   mary with wood and $CH_4$ as feedstocks.
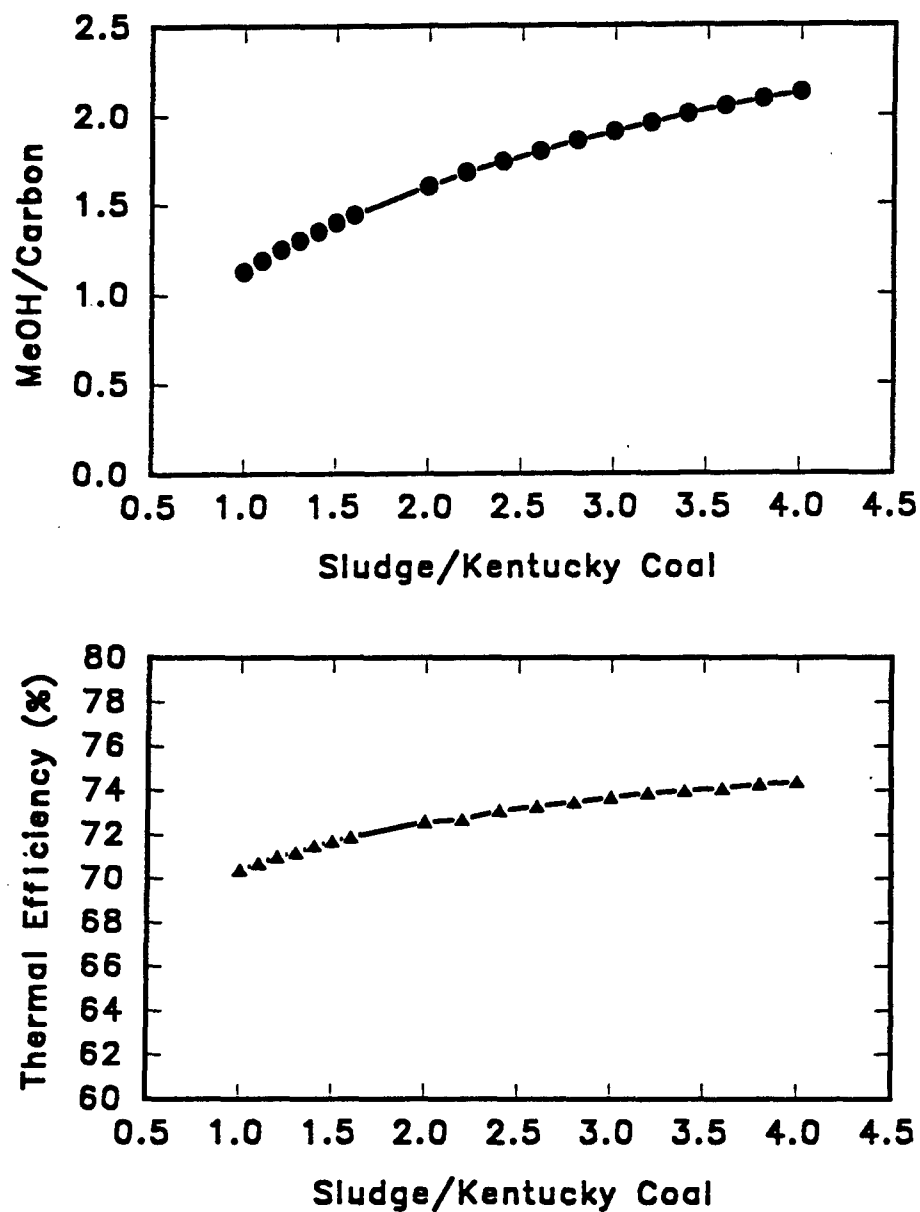
Figure III-4. Plot of Methanol Production and Thermal Efficiency vs. Sludge Feed Rate.

Sludge 2771 kg.h    AR Wood    **\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\***
Lime     694 kg/h    4630 kg/h    **Carbon Conversion in HPR: 90%**
CH4     353 kg/h           **Carbon Efficiency: 73.5%**
DG    3347 kg/h           **Thermal Efficiency: 76.0%**
                                 **\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\*\***

Off Gas
14 kmol/h
CO    2.5
CO2   2.6    H2O       MeOH

**DRYER**
**150 C**

CH4 24.1   934 kg/h 4537 kg/h
H2O   0.1
H2   69.9

Wood 4305 kg/h
5% moist.

**HPR**     947 C

**COND**

**900 C**

**50 C**

C
294 kg/h
Ash
1375 kg/h

900 C
3525 kmol/h
CO    6.3
CO2   0.6
CH4 30.6
H2O   6.3
H2   56.2

50 C
3347 kmol/h

**COMB**

**HE**

260 C
3555 kmol/h
CO     2.3
CO2    2.5
CH4   22.8
H2O    1.5
H2    66.1
MeOH   4.8

Al2O3

Wood
2183 kg,h

**MPR**    1000 C      229 C    **MSR**

**1000 C**            **260 C**

3894 kmol/h
CO    8.5
CO2   0.3
CH4 20.8
H2O   3.4

C 2032 kg/h   H2   67.0

Figure III-5. Data summary with wood, sludge, CH₄, and digester gas as feedstocks.

Appendix III-1 Computer Printout with Wood and $CH_4$ as Feedstocks.

Remarks: AW100+G15/CTW

CPU Time (min): 2.72

FEEDSTOCKS:

    No. 1      Name: Wood
        PROCESS CAPACITY (AR tons/cd): 100
        AR COMPOSITION (wt%):
                    C: 45.86
                    H: 5.27
                    O: 36.07
                  H2O: 11.67
                  ASH: .66
                    S: .04
                OTHER: .43
        HEATING VALUE (kcal/kg-MF):-4888.9
        HEAT OF FORMATION (kcal/kg-MAF):-1214.4
        HEAT CAPACITY (kcal/'C*MAFkg): .57
        MOISTURE AFTER DRYING (wt%): 11.67

    OTHER INPUT:   CH4 into HPR (tons/cd): 15
                                (kg/kg-ARfeed#1): .15
                    Digester Gas into HPR (tons/cd): 0
                                        (kg/kg-ARfeed#1): 0
                    H2O in to HPR(tons/cd): 0
                                (kg/kg-ARfeed#1): 0
                    LIMESTONE (tons/cd): .3565728
                    FOR COMBUSTION (tons/cd):
                        Wood: 33.38297

    PRODUCT:   CARBON BLACK (tons/cd): 26.39612
            METHANOL (tons/cd): 68.95502
            GAS (tons/cd): 0

PRODUCT DISTRIBUTION (kg-C/kg-MeOH):0.38

CARBON BLACK YIELD (kg/kg-ARfeed#1): .2639612
MEOH YIELD (kg/kg-ARfeed#1): .6895502
WATER YIELD (kg/kg-ARfeed#1): .133839
OFF GAS (kmol/kg-ARfeed#1): 7.101427E-04
        (kg/kg-ARfeed#1): 5.394378E-03
    FRACTION OF BURNING OFF-GAS (%): 100
    COMPOSITION (vol%):
                CO        2.717432
                CO2       2.987879
                CH4       23.91609
                H2O       8.341512E-02
                H2        69.45669
                CH3OH     .8384966
    TOTAL HEATING VALUE (kcal/h):-334401.4

CONVERSION OF CARBON IN FEEDSTOCK FOR HPR (%): 90
CARBON EFFICIENCY (%): 72.16
THERMAL EFFICIENCY (%): 74.89

BALANCE CHECK:
C IN 202.3981          C OUT 202.3903
H IN 475.2008          H OUT 475.1611
O IN 134.358           O OUT 134.3459


UNIT 1#     HYDROGASIFIER (HPR)

(I)OPERATING CONDITIONS,   Pressure (atm): 50
                           Temperature ('C): 900

(II)INPUT:

  (1)Feedstocks:
    (i)Name: Wood
                Rate (kg/h): 4629.63
                Composition  C% wt: 45.86
                             H% wt: 5.27
                             O% wt: 36.07
                           H2O% wt: 11.67
                           Ash% wt: .66
                             S% wt: .04
                Enthalpy (kcal/h):-6977758
                Temperature ('C): 25

  (2)CH4     Feed Rate (kg/h): 694.4445
                Enthalpy (kcal/h):-774179.9
                Temperature ('C): 25

  (3)Digester Gas    Feed Rate (kg/h): 0
                Enthalpy (kcal/h): 0
                Temperature ('C): 25

  (4)Additional Water    Feed Rate (kg/h): 0
                Enthalpy (kcal/h): 0
                Temperature ('C): 100

  (5)Limestone   Feed Rate (kg/h): 16.508
                Content: CaCO3% wt: 70
                Enthalpy (kcal/h):-33302.16
                Temperature ('C): 25

  (6)Gas Stream <F>    Rate (kmol/h): 2166.787
                Composition (vol%)
                        CO          2.717432
                        CO2         2.987879
                        CH4         23.91609
                        H2O         8.341512E-02
                        H2          69.456·
                        CH3OH       .83849·
                Enthalpy (kcal/h):-2753·
                          at t.·· ('C): 926.5258

(III)OUTPUT:

(1)Ash      Discharge Rate (kg/h): 44.46702
            Enthalpy (kcal/h):-7573.43
                                at temp ('C): 900

(2)Gas Stream <G>    Flow Rate (kmol/h): 2297.939
                     Composition (vol%)
                          CO        6.810789
                          CO2        .6568884
                          CH4       30.06123
                          H2O        6.788135
                          H2        55.68296
                          CH3OH      0
                     Enthalpy (kcal/h):-8119087
                                        at temp ('C): 900

(3)Residue Carbon    Rate (kg/h): 212.3149
                     Enthalpy (kcal/h): 66082.81
                     Heating Value (kcal/h):-1662664

(IV)HEAT LOAD (kcal/h):-16.22302

(V)VALUE OF (H/O): 16.44135

(VI)BALANCE CHECK:
   IN C: 862.399      OUT C: 862.3912
   IN H: 5634.289     OUT H: 5634.249
   IN O: 342.6967     OUT O: 342.6847


            UNIT 2#    METHANE PYROLYZER (MPR)

(I)OPERATING CONDITION,  Pressure (atm): 50
                         Temperature ('C): 1000

(II)INPUT:

   (1)Gas Stream <G>    Rate (kmol/h): 2297.939
                        Composition (vol%)
                             CO        6.810789
                             CO2        .6568884
                             CH4       30.06123
                             H2O        6.788135
                             H2        55.68296
                             CH3OH      0
                        Enthalpy (kcal/h):-8119087
                                           at temp ('C): 900

   (2)Alumina    Rate (kg/h): 63042.24
                 Temperature ('C): 1400

(III)OUTPUT

   (1)Gas Stream <H>    Rate (kmol/h): 2539.77
                        Composition (vol%)
                             CO        9.204524
                             CO2        .3098129
                             CH4       20.4348
                             H2O        3.668596
                             H2        66.38226
                             CH3OH      0

Enthalpy (kcal/h): 116196.7

ta temp ('C): 1000

(2)Carbon Black <M>   Discharge Rate (kg/h): 1222.042

(kmol/h); 101.7521

Enthalpy (kcal/h): 435849.1

at temp ('C): 1000

(3)Alumina     Rate (kg/h): 63042.24

Temperature ('C): 1000

(IV)HEAT LOAD (kcal/h): .2649658

(V)VALUE OF (H/O): 16.44135

(VI)BALANCE CHECK:
    IN C: 862.3912     OUT C: 862.3912
    IN H: 5634.249     OUT H: 5634.249
    IN O: 342.6847     OUT O: 342.6847

UNIT 3#   METHANOL CONVERTER

(I)OPERATING CONDITION,  Pressure (atm): 50

Temperature ('C): 260

(II)INPUT:

(1)Gas Stream <H>     Rate (kmol/h): 2539.77

Composition (vol%)
                CO        9.204524
                CO2       .3098129
                CH4       20.4348
                H2O       3.668596
                H2        66.38226
                CH3OH     0

Enthalpy (kcal/h):-1.710283E+07

at temp ('C): 256.5093

(III)OUTPUT:

(1)Gas Stream <S>     Rate (kmol/h): 2304.104

Composition (vol%)
                CO        2.559359
                CO2       2.814074
                CH4       22.52489
                H2O       1.57125
                H2        65.416.
                CH3OH     5.114038

Enthalpy (kcal/h):-2.033917E+07

at temp ('C): 260

(IV) AT LOAD (kcal/h):-3236343

(V)VALUE OF (H/O): 16.4415

(VI)BALANCE CHECK:
    IN C: 760.6392     OUT C: 760.6391
    IN H: 5634.249     OUT H: 5634.248

IN O: 342.6847      OUT O: 342.6846

## UNIT 4# CONDENSER

(I) OPERATING CONDITION,    Pressure (atm): 50

                      Temperature ('C): 50

(II) INPUT:

   (1) Gas Stream &lt;S&gt;    Rate (kmol/h): 2304.104
                        Composition (vol%)
                           CO       2.559359
                           CO2      2.814074
                           CH4     22.52489
                           H2O      1.57125
                           H2       65.41639
                           CH3OH   5.114038
                      Enthalpy (kcal/h):-2.033917E+07
                                      at temp ('C): 260

(III) OUTPUT:

   (1) Gas Stream &lt;U&gt;    Rate (kmol/h): 2170.074
                        Composition (vol%)
                           CO       2.717432
                           CO2      2.987879
                           CH4     23.91609
                           H2O      8.341512E-02
                           H2       69.45669
                           CH3OH   .8384966
                      Enthalpy (kcal/h):-1.75192E+07
                                      at temp ('C): 50

   (2) MeOH    Rate (kmol/h): 99.63677
                    (kg/h): 3192.362

   (3) H2O    Rate (kmol/h): 34.39304
                    (kg/h): 619.625

(IV) HEAT LOAD (kcal/h):-4668477

(V) VALUE OF (H/O): 24.76298

(VI) BALANCE CHECK:
   IN C: 760.6391      OUT C: 760.6391
   IN H: 5634.248      OUT H: 5634.249
   IN O: 342.6846      OUT O: 342.6846

## UNIT 5# GAS HEAT EXCHANGER

(I) OPERATING CONDITION,  Pressure (atm): 50

(II) INSIDE
      (1) Gas In &lt;H&gt;    Rate (kmol/h): 2539.77
                      Temp ('C): 1000
                      Enthalpy (kcal/h): 116196.7

        (2)Gas Out &lt;H&gt;  Rate (kmol/h): 2539.77
                        Temp ('C): 256.5093
                        Enthalpy (kcal/h):-1.710283E+07

(III)OUTSIDE
        (1)Gas In &lt;F&gt;  Rate (kmol/h): 2166.787
                        Temp ('C): 50
                        Enthalpy (kcal/h):-1.749266E+07

        (2)Gas Out &lt;F&gt;  Rate (kmol/h): 2166.787
                        Temp ('C): 926.5258
                        Enthalpy (kcal/h):-275321.9

(IV)HEAT LOAD (kcal/h):-1689.224

## UNIT 6# COMBUSTOR

(I)INPUT:

  (1)Residual Char (kg/h): 212.3149

  (2)Off Gas (kmol/h): 3.287698

  (3)Air (kmol/h): 16.00207

  (4)Alumina (kg/h): 63042.24

  (5)Wood(kg/h): 1545.508

(II)OUTPUT:

  (1)Flue Gas (kmol/h): 19.28977 (approx.)

  (2)Alumina (kg/h): 63042.24

(III)HEAT LOAD (kcal/h):-8671133

Remarks: 5W100+5S70+G15+D35

CPU Time (min): 5.88

FEEDSTOCKS:

    No. 1        Name: Wood
        PROCESS CAPACITY (AR tons/cd): 100
        AR COMPOSITION (wt%):
                    C: 45.86
                    H: 5.27
                    O: 36.07
                  H2O: 11.67
                  ASH: .66
                    S: .04
                OTHER: .43
        HEATING VALUE (kcal/kg-MF):-4888.9
        HEAT OF FORMATION (kcal/kg-MAF):-1214.4
        HEAT CAPACITY (kcal/'C*MAFkg): .57
        MOISTURE AFTER DRYING (wt%): 5

    No. 2        Name: Sludge (Riverside)
        PROCESS CAPACITY (AR tons/cd): 70
        AR COMPOSITION (wt%):
                    C: 28.55
                    H: 4.09
                    O: 16.03
                  H2O: 9.82
                  ASH: 36.53
                    S: 1.36
                OTHER: 3.62
        HEATING VALUE (kcal/kg-MF):-3061.1
        HEAT OF FORMATION (kcal/kg-MAF):-1769.7
        HEAT CAPACITY (kcal/'C*MAFkg): .25
        MOISTURE AFTER DRYING (wt%): 5

OTHER INPUT:   CH4 into HPR (tons/cd): 15
                         (kg/kg-ARfeed#1): .15
               Digester Gas into HPR (tons/cd): 35
                                 (kg/kg-ARfeed#1): .35
               H2O in to HPR(tons/cd): 0
                         (kg/kg-ARfeed#1): 0
               LIMESTONE (tons/cd): 8.843006
               FOR COMBUSTION (tons/cd):
                    Wood: 48.97242

PRODUCT:   CARBON BLACK (tons/cd): 46.57304
           METHANOL (tons/cd): 101.964
           GAS (tons/cd): 0

PRODUCT DISTRIBUTION (kg-MeOH/kg-C): 2.19

CARBON BLACK YIELD (kg/kg-ARfeed#1): .4657304
MEOH YIELD (kg/kg-ARfeed#1): 1.01964
WATER YIELD (kg/kg-ARfeed#1): .2113636
OFF GAS (kmol/kg-ARfeed#1): 3.458929E-03
       (kg/kg-ARfeed#1): 2.555812E-02
       (kmol/h): 16.01356
   PURGE FRACTION (%): .452814
  FRACTION OF BURNING OFF-GAS (%): 100
  COMPOSITION (vol%):

|        |              |
|--------|--------------|
| CO     | 2.444442     |
| CO2    | 2.597323     |
| CH4    | 24.13597     |
| H2O    | 8.682551E-02 |
| H2     | 69.90885     |
| CH3OH  | .8265951     |

  TOTAL HEATING VALUE (kcal/h):-1637921

CONVERSION OF CARBON IN FEEDSTOCK FOR HPR (%): 90
CARBON EFFICIENCY (%): 73.68
THERMAL EFFICIENCY (%): 76.03

BALANCE CHECK:

| C IN 331.6794 | C OUT 331.6683 |
|---------------|----------------|
| H IN 736.4289 | H OUT 736.3698 |
| O IN 203.0361 | O OUT 203.0176 |

### UNIT 1#   HYDROGASIFIER (HPR)

(I) OPERATING CONDITIONS,  Pressure (atm): 50
                               Temperature ('C): 900

(II) INPUT:

  (1) Feedstocks:
     ( 1 )Name: Wood
         Rate (kg/h): 4304.581
         Composition  C% wt: 49.32299
                    H% wt: 5.66795
                    O% wt: 38.79373
              H2O% wt: 5
              Ash% wt: .7098382
                S% wt: 4.302049E-02
        Enthalpy (kcal/h):-5257743
        Temperature ('C): 150

     ( 2 )Name: Sludge (Riverside)
         Rate (kg/h): 3076.316
         Composition  C% wt: 30.07596
                    H% wt: 4.308605
                    O% wt: 16.88678
              H2O% wt: 5
              Ash% wt: 38.48248
                S% wt: 1.43269
         Enthalpy (kcal/h):-3452120
        Temperature ('C): 150

  (2) CH4    Feed Rate (kg/h): 694.4445
             Enthalpy (kcal/h):-774179.9

                    Temperature ('C): 25

    (3) Digester Gas      Feed Rate (kg/h): 1620.37
                          Enthalpy (kcal/h):-2845242
                          Temperature ('C): 25


    (4) Additional Water   Feed Rate (kg/h): 0
                           Enthalpy (kcal/h): 0
                           Temperature ('C): 100


    (5) Limestone    Feed Rate (kg/h): 409.3984
                     Content: CaCO3% wt: 70
                     Enthalpy (kcal/h):-825893.6
                     Temperature ('C): 25


    (6) Gas Stream <F>    Rate (kmol/h): 3520.441
                         Composition (vol%)
                             CO        2.444442
                             CO2       2.597323
                             CH4       24.13597
                             H2O       8.682551E-02
                             H2        69.90885
                             CH3OH     .8265951
                         Enthalpy (kcal/h): 1727492
                                        at temp ('C): 947.3911


(III) OUTPUT:

    (1) Ash    Discharge Rate (kg/h): 1559.402
               Enthalpy (kcal/h):-138272.5
                                  at temp ('C): 900


    (2) Gas Stream <G>    Flow Rate (kmol/h): 3704.471
                         Composition (vol%)
                             CO        6.23228
                             CO2       .5500355
                             CH4       30.68466
                             H2O       6.275629
                             H2        56.2574
                             CH3OH     0
                         Enthalpy (kcal/h):-1.138444E+07
                                        at temp ('C): 900


    (3) Residue Carbon   Rate (kg/h): 304.838
                         Enthalpy (kcal/h): 94880.56
                         Heating Value (kcal/h):-2387225


(IV) HEAT LOAD (kcal/h):-147.7762

(V) VALUE OF (H/O): 18.21008

(VI) BALANCE CHECK:
     IN C: 1387.964      OUT C: 1387.953
     IN H: 9179.912      OUT H: 9179.854
     IN O: 504.1222      OUT O: 504.1037



            UNIT 2#   METHANE PYROLYZER (MPR)


(I) OPERATING CONDITION,  Pressure (atm): 50

Temperature ('C): 1000

(II) INPUT:

   (1) Gas Stream <G>   Rate (kmol/h): 3704.471
                        Composition (vol%)

| | |
|---|---|
| CO | 6.23228 |
| CO2 | .5500355 |
| CH4 | 30.68466 |
| H2O | 6.275629 |
| H2 | 56.2574 |
| CH3OH | 0 |

                        Enthalpy (kcal/h):-1.138444E+07
                                       at temp ('C): 900

   (2) Alumina    Rate (kg/h): 100446.7
               Temperature ('C): 1400

(III) OUTPUT

   (1) Gas Stream <H>   Rate (kmol/h): 4091.234
                        Composition (vol%)

| | |
|---|---|
| CO | 8.414859 |
| CO2 | .2589349 |
| CH4 | 20.86308 |
| H2O | 3.388828 |
| H2 | 67.0743 |
| CH3OH | 0 |

                        Enthalpy (kcal/h): 1662475
                                  ta temp ('C): 1000

   (2) Carbon Black <M>   Discharge Rate (kg/h): 2156.159
                             (kmol/h); 179.5303
                    Enthalpy (kcal/h): 769007.8
                                  at temp ('C): 1000

   (3) Alumina    Rate (kg/h): 100446.7
               Temperature ('C): 1000

(IV) HEAT LOAD (kcal/h): 7.686876E-02

(V) VALUE OF (H/O): 18.21008

(VI) BALANCE CHECK:

| | |
|---|---|
| IN C: 1387.953 | OUT C: 1387.953 |
| IN H: 9179.854 | OUT H: 9179.854 |
| IN O: 504.1037 | OUT O: 504.1037 |

UNIT 3#   METHANOL CONVERTER

(I) OPERATING CONDITION,   Pressure (atm): 50
                                     mperature ('C): 260

(II) INPUT:

   (1) Gas Stream <H>   Rate (kmol/h): 4091.234
                        Composition (vol%)

| | |
|---|---|
| CO | 8.414859 |
| CO2 | .2589349 |

```
                              CH4       20.86308
                              H2O       3.388828
                              H2        67.0743
                              CH3OH     0
                    Enthalpy (kcal/h):-2.706722E+07
                                        at temp ('C): 228.2895
```

**(III) OUTPUT:**

```
    (1)Gas Stream <S>    Rate (kmol/h): 3738.103
                         Composition (vol%)
                              CO        2.312579
                              CO2       2.457213
                              CH4       22.83398
                              H2O       1.535146
                              H2        66.13769
                              CH3OH     4.723396

                    Enthalpy (kcal/h):-3.094903E+07
                                        at temp ('C): 260
```

**(IV) HEAT LOAD (kcal/h):-3881819**

**(V) VALUE OF (H/O): 18.21025**

**(VI) BALANCE CHECK:**

```
    IN C: 1208.423      OUT C: 1208.423
    IN H: 9179.854      OUT H: 9179.854
    IN O: 504.1037      OUT O: 504.1037
```

**UNIT 4# CONDENSER**

**(I) OPERATING CONDITION,    Pressure (atm): 50**

**Temperature ('C): 50**

**(II) INPUT:**

```
    (1)Gas Stream <S>    Rate (kmol/h): 3738.103
                         Composition (vol%)
                              CO        2.312579
                              CO2       2.457213
                              CH4       22.83398
                              H2O       1.535146
                              H2        66.13769
                              CH3OH     4.723396
                    Enthalpy (kcal/h):-3.094903E+07
                                        at temp ('C): 260
```

**(III) OUTPUT:**

```
    (1)Gas Stream <U>    Rate (kmol/h): 3536.455
                         Composition (vol%)
                              CO        2.444442
                              CO2       2.597323
                              CH4       24.13597
                              H2O       8.682551E-02
                              H2        69.90885
                              CH3OH     .8265951
```

Enthalpy (kcal/h):-2.712234E+07
                                    at temp ('C): 50

    (2)MeOH     Rate (kmol/h): 147.3333
                      (kg/h): 4720.558

    (3)H20    Rate (kmol/h): 54.3148
                  (kg/h): 978.5354

(IV)HEAT LOAD (kcal/h):-7473811

(V)VALUE OF (H/O): 28.04342

(VI)BALANCE CHECK:
    IN C: 1208.423      OUT C: 1208.423
    IN H: 9179.854      OUT H: 9179.854
    IN O: 504.1037      OUT O: 504.1037


UNIT 5# GAS HEAT EXCHANGER

(I)OPERATING CONDITION,  Pressure (atm): 50

(II)INSIDE
    (1)Gas In <H>     Rate (kmol/h): 4091.234
                      Temp ('C): 1000
                      Enthalpy (kcal/h): 1662475

    (2)Gas Out <H>    Rate (kmol/h): 4091.234
                      Temp ('C): 228.2895
                      Enthalpy (kcal/h):-2.706722E+07

(III)OUTSIDE
    (1)Gas In <F>     Rate (kmol/h): 3520.441
                      Temp ('C): 50
                      Enthalpy (kcal/h):-2.699952E+07

    (2)Gas Out <F>    Rate (kmol/h): 3520.441
                      Temp ('C): 947.3911
                      Enthalpy (kcal/h): 1727492

(IV)HEAT LOAD (kcal/h):-2674.644


UNIT 6# COMBUSTOR

(I)INPUT:

   (1)Residual Char (kg/h): 304.838

   (2)Off Gas (kmol/h): 16.01356

   (3)Air (kmol/h): 78.41016

   (4)Alumina (kg/h): 100446.7

   (5)Wood (kg/h): 2267.242

(II)OUTPU

Appendix III-2  Computer Printout with Wood, Sludge, CH$_4$ and Digester Gas as Feedstocks.
(cont'd)

    (1)Flue Gas (kmol/h): 94.42373 (approx.)

    (2)Alumina (kg/h): 100446.7

 (III)HEAT LOAD (kcal/h):-1.381593E+07

# APPENDIX A

## Quality Control Evaluation Report

The experimental measurements reported in this document were obtained with the use of the Brookhaven Tubular Reactor Facility. The design, construction operation and a description of the measurement equipment and instrumentation was initially reported in Brookhaven National Laboratory Report No. 50698, "Design, Construction, Operation and Initial Results of a Flash Hydropyrolysis Experimental Unit," by Peter Fallon and Meyer Steinberg (January 1977). The construction procedures and instrumentation used were in accordance with best practices available for this type of experiment. A Safety Analysis Report on the Brookhaven Hydropyrolysis Experimental Equipment was written in November 1991 to requalify and obtain approval from the Brookhaven National Laboratory Safety Committee for operation. Since initial construction and operation, the equipment has been requalified twice, the latest being November 1991, just before performing the experiments reported herein.

The facility contains the following measuring equipment: thermocouple temperature monitoring and control, pressure indicating and control, volumetric flow meter, and on-line gas chromatograph for determining the gaseous component concentration.

The temperature and pressure instrumentation were checked against secondary standards which were in turn calibrated against primary standards. The precision of temperature measurements was $\pm 5°C$. The precision of pressure measurement was within $\pm 5$ psi. The on-line gas chromatograph was calibrated before each run using standard gas calibrating gases obtained from vendors with certification. The gases monitored included $H_4$, $C_2H_6$, CO and $CO_2$. The precision of the chromatograph calibration is estimated to be $\pm 5\%$ of the gas component concentration.

The feedstock composition of samples of biomass were analyzed in duplicate by Commercial Testing and Engineering Co., Lombard, Illinois, in accordance with well-established analytical procedures.

The mass balances after the flow runs with this tubular reactor facility could be made with an accuracy of within ±5%.

## TECHNICAL REPORT DATA
*(Please read Instructions on the reverse before completing)*

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15. SUPPLEMENTARY NOTES AEERL project officer is Robert H. Borgwardt, Mail Drop 63, 919/541-2336. (*)Hydrocarb Corp., 232 W. 40th St., New York, NY 10018.

16. ABSTRACT The report provides experimental and process design data in support of studies for developing the coprocessing of fossil fuels with biomass by the Hydrocarb process. The experimental work includes the hydropyrolysis of biomass and the thermal decomposition of methane in a 2.44 m long tubular flow reactor with a 25.4 mm inside diameter. The rates of reaction and conversion were obtained at temperature and pressure conditions pertaining to a Hydrocarb process design. A process simulation computer model was used to optimize the process configuration and obtain energy and mass balances. Multiple feedstocks were evaluated, including biomass with natural gas and biomass with coal. Additional feedstocks (including sewage sludge and digester gas) were evaluated for a pilot plant unit. Under conditions of rapid heat up, high temperatures, and high hydrogen pressure, hydrogasification of biomass is especially effective in producing carbon monoxide and methane. An overall conversion of 88-90 wt % of biomass was obtained. At 800 C and 51 atm (5166 kPa) pressure, the initial rate of biomass conversion to gases is 92% per min. The reaction rate of methane decomposition in the same tubular reactor was investigated at between 700 and 900 C, with pressures from 28 to 56 atm (2836 to 5673 kPa).

| 17. | KEY WORDS AND DOCUMENT ANALYSIS | |
|---|---|---|
| a. DESCRIPTORS | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
| Pollution<br>Fossil Fuels<br>Biomass<br>Pyrolysis<br>Methane<br>Carbon Monoxide | Pollution Control<br>Stationary Sources<br>Hydrocarb Process<br>Hydropyrolysis | 13B<br>21D<br>06C<br>07D<br>07C<br>07B |

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